

**A SOFTWARE PACKAGE FOR
CARBON-14 DATING**

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November 1991**

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Abstract

In processing data pertaining to the radiocarbon dating context, there are many statistical methods which may be applied in the treatment of data, all of which are usually intended to produce reliable radiocarbon ages. In the pursuit of a suitable treatment of data, this work has produced some new methods in managing radiocarbon data. A major feature which is developed here is the incorporation of a certain number of statistical quality controls into the data management process. The culmination of this work is the presentation of a software package which has been successfully employed for over 6 years at the Scottish Universities Research and Reactor Centre at East Kilbride.

The work can be described according to the various sections of this report. There are 8 sections in this report altogether. Section 1 is an introduction to the work and provides a brief description of the radiocarbon dating principle with particular emphasis on the liquid scintillation approach. Aspects of the method are examined including some basic axioms which give rise to the method, the chemistry of the liquid scintillation method and some statistical avenues which have already been explored in the pursuit of refining the production of radiocarbon ages.

In section 2 some preliminary tests are conducted on a number of background counting samples. Two simple tests are conducted: a limited test for correlation patterns in the background counting data; a test for the normality of the background counting data.

The problem of outliers in counting data is examined next in section 3. With an aim to filtering out spurious counting data, a method is developed here for small data samples which screens the data for the presence of outliers and removes them on discovery. The method is extremely simple and is based on the linear regressions of the estimated percentage points

of two outlier detection statistics on the natural logarithms of sample sizes. Its simplicity makes it relatively easy to program which is the advantage of the method.

In section 4 a new way of estimating the background activity using a pool of background samples is developed. The estimation, which is referred to as retrospect estimation, essentially involves drawing on a knowledge of the history of the samples and through that knowledge making corrections in the data which assist in the production of a mean background activity.

Section 5 explores an alternative method for calculating the radiocarbon age of a sample. This method considers the correlation introduced into the counting data once corrections for the background activity have been applied to that data. The method basically involves deriving a weighted least squares estimate of the sample age taking into account the correlation introduced by the corrections for background. Section 6 follows this up with a simulation study which seeks to compare the alternative method of age estimation with a conventional method and finds favour for the alternative method.

In section 7 there is a useful description of the software package which encapsulates some of the work presented in this report. The final section presents some brief conclusions and looks at possibilities for future modification and expansion of the software.

This work is by no means a complete or definitive work since it would be virtually impossible to exhaust all possible treatments of radiocarbon data. What is achieved, instead, is a software package which covers a selected range of statistical aspects in radiocarbon dating and which hopefully produces reliable radiocarbon ages which is the primary aim of the radiocarbon method.

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Acknowledgements

I would like to thank the following people for their support:

- my two supervisors Mr. Tom Aitchison and Dr. Murdoch Baxter for being both helpful and patient towards me in equal measures;
- Dr. Gordon Cook, Dr. Mike Stenhouse and Dr. Marian Scott for their generous assistance in this work;
- Prof. Mike Titterington for the opportunity to participate in this work and to all in the statistics department who gave me valuable input at various times;
- my charitable sponsors in the form of the Science & Engineering Research Council;
- Mr. Jim Richmond of the Turing Institute who provided me with both the time and the facilities to produce this piece of work;
- Dr. George Gettingby of the statistics department at Strathclyde University for some much needed and much appreciated encouragement;
- my helper and friend Jesus Christ for the strength to complete this work and without whom it would not have been completed.

My hope is that the results which have been achieved by this work might be utilised and extended by others. I owe it to those people who were generous in their time and assistance to translate this work into some kind of presentable form. So here it is.

Alister T. Hooke

November, 1991.

1 Introduction

This introduction provides a broad and simplified overview of the radiocarbon dating method with particular reference to the liquid scintillation counting method. The results of this work, however, are not necessarily confined to the liquid scintillation context and may be useful in gas counting and accelerator mass spectrometric contexts since the results are concerned with statistical theory in the general management of carbon-14 data. There is no attempt here to provide a comprehensive historical background to the subject of radiocarbon dating. The background supplied in this introduction is merely sufficient for a basic understanding of the content of this report.

1.1 General Aim

The general aim of this report is to present the methods and reasoning contained in the two computer programs which emerged from this work. This will help in the assessment of their validity and usefulness. The report essentially leads up to these programs and serves to be a validation of them.

The research effort was initially directed on the chemistry side by Dr. Mike Stenhouse of the Glasgow University radiocarbon dating laboratory. (At the stage of writing the laboratory has for some time been relocated to the Scottish Universities Research and Reactor Centre at East Kilbride.) The primary concern expressed by Dr. Stenhouse was the provision of a computer software facility for the dating procedure. This was required since a new counting system — a Packard 4530 liquid scintillation counter — had just been installed prior to this work and the software associated with the old system was not compatible with

the new system.

Not only was a new software facility required but it was also required that the new facility be superior to the old one. System improvement, however, is generally an open-ended affair and no claim is made in this report for completeness. Thus there is plenty of scope to extend the work that is presented here although it is hoped that this work goes a considerable way to achieving system improvement.

1.2 Specific Aims

With the general aim in mind, the specific aims of this work can now be presented. These aims are :-

- to improve statistical aspects of the dating procedure by providing safeguards against anomalous data and by producing better estimates of relevant statistical parameters;
- to translate these improvements into suitable software;
- to suggest further improvements not pursued in this work which would augment what is already hopefully achieved by this work.

These three aims constitute the entire basis and content of this report.

1.3 Physical Background

In 1947 Anderson et al. [4] achieved an important scientific breakthrough which turned out to be the springboard for the emergence of the modern radiocarbon dating method. This group of researchers was the first to experimentally demonstrate the existence of naturally occurring radiocarbon — the chemical symbol is ^{14}C .

1.3.1 Physical Processes

Two key physical processes underlie the principle of radiocarbon dating. The first of these processes is known as the dynamic carbon cycle. This is the exchange of carbon that takes place between the atmosphere and the biosphere. It is assumed, provisionally, that all lifeforms absorb and release carbon during their lifetime such that a constant $^{14}\text{C}/^{12}\text{C}$ ratio is maintained and that this ratio is the same for recent and past lifeforms. This assumes that the atmospheric carbon reservoir has always facilitated a constant $^{14}\text{C}/^{12}\text{C}$ ratio.

The second key process is the decay of ^{14}C . In this process, radiocarbon decays to nitrogen with the emission of a β -particle. The decay rate for ^{14}C is expressed in terms of its half-life and this is known to be around 5730 years [25]. This decay rate is of importance because the knowledge of a sample's ^{14}C activity can be used to determine the time lapsed since death — the point at which the sample would have ceased to assimilate carbon from the atmosphere — and thus determine the radiocarbon age of the sample. (A sample might constitute a piece of bone, a section from a tree, some peat core, charcoal from early man's fire, etc.)

It can now be stated that the assumption of a constant $^{14}\text{C}/^{12}\text{C}$ ratio is incorrect but can be compensated for.

1.3.2 Variations in the $^{14}\text{C}/^{12}\text{C}$ Ratio

In 1958 De Vries [20] carried out some tree-ring studies on some 18th century wood. Over the 100 year period 1700–1800 A.D. two different types of trees were measured with respect to selected tree-ring samples. The data revealed fluctuations of up to 2% in the atmospheric

^{14}C during the relevant time interval, the patterns of variation being similar for the two trees examined. Other work by Willis et al. [56] on a specimen of *Sequoia gigantea* also revealed similar sized variations over a 1200 year period.

These initial demonstrations of ^{14}C variations suggested a need for further investigation over a broader interval of time. This need was first adequately met by Ferguson and co-workers [21, 22, 23] in the late 60's with the construction of the Bristlecone Pine chronology. Stretching back over 7000 years, this chronology demonstrated the relationship between the ^{14}C and true ages of a considerable number of samples of *Pinus aristata*.

The chronology revealed a slow, long-term sinusoidal variation. This has very likely been fashioned by the earth's magnetic field [12]. The existence and interpretation of this long-term variation was undisputed but controversial suggestions about short-term variations were also being promoted at the same time [48, 49]. Controversy surrounded the number and interpretation of these latter variations. A problem they posed was that they introduced non-uniqueness between the ^{14}C and true ages.

Suess, the principle advocator at that time of short-term variations, referred to these variations as "wiggles". It was really the later development of high precision radiocarbon dating laboratories, however, that served to confirm the existence of wiggles [34]. A major source of these short-term fluctuations has been attributed to solar activity [18].

The variations described above, both long-term and short-term, may be classified as natural ^{14}C variations according to their given interpretations. Other studies have examined significant man-made ^{14}C variations which have been induced through pivotal historical and anthropological developments. The first significant man-made variation came through the advent of the industrial revolution which through the large scale burning of fossil fuels

released vast amounts of ^{14}C free CO_2 into the atmosphere [24, 47]. The second significant man-made variation came through the nuclear bomb testing period in the early 60's which undoubtedly increased ^{14}C levels [41, 42].

1.3.3 The Calibration Problem

The existence of ^{14}C variations, both long-term and short-term, demands a suitable calibration in order to properly refer ^{14}C dates to the true calendar time-scale. The high precision chronology developed by Stuiver and Pearson among others [37, 44] is currently the definitive calibration chronology, superseding the earlier Bristlecone Pine chronology.

Even with the high precision chronology there still remains the question of how to deal with wiggles and the degree to which they are truly present in the data. Many people have adopted various regression methods in addressing this problem. Clark, for instance, adopts a smooth regression approach in which a curve, specified only with respect to its smoothness, is fitted to the calibration data [14]. This effectively plays down the presence of wiggling in the data. Suess, on the other hand, adopts an ultra-sensitive regression approach with both his original hand-drawn curve and subsequent spline curves [50]. Other regression approaches exist besides those of Clark and Suess but these two provide a good contrast in calibration methods using regression.

There is also the question of how to combine errors of the ^{14}C data with the errors of the regression curves. These two errors need to be specified and then suitably combined in the calculation of true calendar ages. This problem has been examined by Aitchison and Scott [1].

An answer to the overall calibration problem, however, is not pursued in this research effort. It is mentioned because of its importance to radiocarbon dating as a whole.

1.4 Chemical Procedures

A very basic outline of chemical procedures employed in the liquid scintillation method is provided here. A more comprehensive account of these procedures is provided by Scott [39]. Only a brief description is given here in order to convey the derivation of concepts discussed in this report. It should be noted here that the conversion of sample carbon to benzene followed by liquid scintillation counting was the technique used throughout.

1.4.1 Description of Samples

There are four relevant classes of samples:

(a) *field samples* —

These are samples for which we require estimates of true ages. When discussing the age of a sample it will always be the case that the sample being referred to is a field sample. They are sometimes, although not exclusively, samples that have been collected on archaeological field expeditions. This is the reason for the term 'field' although it may be the case that the samples have been collected in a context unrelated to archaeology. There is always a sense, however, in which it can be said that such samples are collected 'from the field'. If the context is an archaeological one, then the archaeologists are undoubtedly interested in determining the dates of their finds perhaps to estimate the age of some ancient civilisation.

(b) *modern standard samples* —

These samples provide a measure of natural ^{14}C activity in the biosphere. The most commonly used modern standard is oxalic acid supplied by the National Bureau of Standards (NBS). In 1958 it was observed that 0.95 times the ^{14}C activity of an oxalic acid standard was equal to the decay-corrected activity of 1890 wood [11]. This wood is regarded as the primary standard since it is considered to have an inherently natural ^{14}C activity. A more recent oxalic acid standard has been developed. It was found that 0.7459 times its ^{14}C activity is equal to the primary standard [45]. This standard — oxalic acid II — is also supplied by the NBS. The standard used in this research is the oxalic I standard although the programs presently work with the new standard. Other modern standards have been developed and used but are not so universally employed as the oxalic standard, including a barium carbonate standard used by Angiolini and Albero [5] and a sucrose standard used by the ANU laboratory at Canberra [28].

(c) *background samples* —

These samples are from extremely old carbon sources, i.e. they contain no radiocarbon. They are required for the evaluation of background activity during liquid scintillation counting. This activity is always present and is due to sources of electron activity other than ^{14}C β -particle emission such as electron activity induced by gamma rays and cosmic rays. These rays tend to interact with the vials containing the sample solutions as well as with the photo-multiplier tubes that are used in the counting process. Discussion of background sample types employed in liquid scintillation counting is deferred until section 2.1.

(d) *spiked samples* —

These samples possess relatively high and known ^{14}C activities. They are used for monitoring the stability of the system and for determining quenching (see section 1.4.4).

All of the above samples are normally present in each run of the dating procedure and in any one run are referred to collectively as a 'batch'.

1.4.2 Synthesis of Benzene

Samples must undergo synthesis to benzene before ^{14}C analysis. This is required for liquid scintillation counting. Benzene is used for a considerable number of reasons: it is composed of 92% carbon; it is relatively stable due to its closed cyclic structure; it can be produced entirely from the sample carbon; it has excellent liquid scintillation counting properties. Switzer [51] also encourages trust in the use of benzene by reporting that low levels of impurity can be attained for benzene used in radiocarbon dating.

The exact method of benzene synthesis may vary from one laboratory to another but the four stages of benzene synthesis presented below are general procedures. These stages are :-

- (a) **sample pretreatment** — this stage is required to prevent contamination of samples through non-contemporary carbon sources. Raw samples often contain non-contemporary carbon sources in them, e.g. the humic acids found in soils can be present in buried charcoal samples. Samples undergo a series of alkali and acid extractions in order to remove non-contemporary material.

- (b) **sample combustion** — after pretreatment the sample is combusted in a CO_2 -free, oxygen rich environment within a stainless-steel reaction vessel in order to produce CO_2 . A minimum amount of sample would normally be used to ensure a yield of benzene constituting at least the optimal weight of sample benzene required for counting. The CO_2 is then cooled, trapped by liquid nitrogen for collection and transferred to a suitable storage system.
- (c) **acetylene synthesis** — the next step is to convert the CO_2 to C_2H_2 (acetylene). A small portion of CO_2 is drawn off for the purpose of estimating fractionation (see section 1.4.5). The remaining CO_2 is brought into contact with molten lithium to produce lithium carbide. Following a cooling period, the lithium carbide undergoes hydrolysis with water to produce acetylene.
- (d) **benzene synthesis** — the final stage involves cyclotrimerising the C_2H_2 to C_6H_6 (benzene). This entails bringing the acetylene into contact with the active sites of a chromium-based catalyst. The resultant benzene is then collected and sealed in a vial with suitable scintillants ready for counting.

1.4.3 Scintillation Counting

When β -particles are released during nuclear decay their energy is released and dissipated into the surrounding environment. The counting method basically exploits this simple fact.

An important factor in the counting process is the provision of a suitable environment in which sample ^{14}C activity can be detected. In liquid scintillation counting, the sample benzene is mixed with a suitable scintillation cocktail or scintillants are dissolved directly

into the benzene. In this environment, detection of sample ^{14}C activity is made possible by a sequence of physico-chemical reactions in the solution: firstly, β -particle energy is transmitted to solvent molecules; secondly, excited solvent molecules transmit energy directly or via other solvent molecules to scintillator molecules; thirdly, excited scintillator molecules release photons of light at a characteristic wavelength.

The light from the scintillator is then converted into electrical energy by means of two photomultiplier tubes (PMT). The tube faces have a photosensitive cathode which produces photoelectrons when struck by light of a particular wavelength. This results in a chain-reaction of increasing electron emission between a sequence of electrodes until a sufficient number are emitted in order to generate an electrical pulse at a final electrode.

A large component of the background activity is removed by the use of the two tubes. If pulses are not detected simultaneously by both tubes, then they are presumed to be thermal noise or other events not generated by ^{14}C decay and consequently rejected.

Any electrical pulse which registers simultaneously in both tubes is subsequently fed to three independent counting channels each set at different discriminator settings of the energy spectrum. These channels each pertain to a unique interval or window of the energy spectrum. Two of them are generally non-overlapping windows while the third channel tends to cover a very broad region of the energy spectrum.

When a pulse is registered in a counting channel it constitutes a single count. These counts and the time over which they are measured are used to estimate the sample ^{14}C activity which is required to produce an estimate for the radiocarbon age of a sample. The pulses are recorded and collectively form pulse amplitudes which show the spectral distribution of detected energy over the windows.

1.4.4 Quenching

Quenching is any phenomenon which reduces the conversion efficiency of the β -particle energy to the electrical pulse amplitudes produced by the PMT. In the perfect counting process all β -particle energy would be converted to photon energy and all photon energy would be converted to electrical energy. This ideal does not exist due to certain factors which inhibit the process.

Inhibition occurs in the conversion of β -particle to photon energy. The greater part of the β -particle energy is picked up and converted to photon energy by scintillator molecules but a fraction of the beta energy is absorbed and retained by solvent molecules and impurities in the benzene. Scintillants can also act as quenching agents. This particular kind of quenching is known as chemical quenching. Inhibition also occurs in the conversion of photon to electrical energy. This is due to the fact that a change in light transmission can result when mixing the sample with the scintillation cocktail or scintillants. A change in the colour of the solution through the mixing of its components can alter the shape of the spectral distribution of detected events. This effect is known as optical or colour quenching. Chemical and colour quenching both tend to result in the depletion of detected events, this being registered as a reduction in the amplitude of detected pulse heights.

To compensate for quenching, some kind of quench correction needs to be applied to the raw counting data. Several methods are available in order to undertake such correction but the method relevant to this study is known as the *external standard technique*. This technique uses an external source of radiation placed next to the vial prior to counting. Gamma radiation from this source is passed for a brief period of time through the sample resulting in high level electron emission according to the Compton collision process. The

scintillations are measured to produce a spectral distribution of pulse heights proportional to the Compton energy. (The sample beta scintillations are negligible compared to the Compton scintillations and can safely be ignored.) With quenching present the spectral distribution of the Compton energy is shifted toward the lower energy region and the degree of shifting is dependent upon the degree of quenching present in the sample. A measure corresponding to this spectral shift known as the *spectral index of the external standard* — or sie value for short — is obtained for the sample. Since the spectral shift in the Compton energy can be shown to be proportional to the spectral shift of the beta energy, the sie value may consequently be used to estimate a quench correction value for the sample.

The estimation of a quench correction value requires a standard. This is achieved by using a series of quenched standards — these are the spiked samples which possess known ^{14}C activities. Once a baseline has been determined for this series, the sie values of all other samples can then be compared with that of the baseline and from this comparison quench correction values can be estimated for all samples. Details of the estimation of quench correction are presented in section 7.2.1.

1.4.5 Fractionation

Fractionation arises as a result of the difference in physico-chemical properties between isotopes of an element. In 1953 an important study of carbon isotopes was conducted by Craig [15]. Differences between isotopes can manifest themselves in small changes of the isotopic ratios during physical and chemical processes, e.g. in processes such as photosynthesis. Craig [16] went on to demonstrate an approximate 2% discrepancy between $^{13}\text{C}/^{12}\text{C}$

ratios in plants and the atmosphere.

Since the ^{14}C – ^{12}C mass difference is double that for the ^{13}C – ^{12}C mass difference, it is assumed that the fractionation effect for ^{14}C is double that for ^{13}C . All measured ^{14}C activities are adjusted for fractionation according to the measured $^{13}\text{C}/^{12}\text{C}$ ratios.

The $^{13}\text{C}/^{12}\text{C}$ ratios are measured from portions of CO_2 taken from the samples. The ratios are quoted as relative rather than absolute enrichments. These are expressed as

$$\delta^{13}\text{C} = \left[\frac{R_S}{R_R} - 1 \right] \times 1000 \text{ ‰}$$

where

$$R_S = {}^{13}\text{C}/^{12}\text{C} \text{ ratio in sample}$$

$$R_R = {}^{13}\text{C}/^{12}\text{C} \text{ ratio in standard}$$

The primary standard used in isotopic fractionation measurement is CO_2 prepared from calcium carbonate. Data in this study are quoted relative to the PDB carbonate standard [17]. In practice, since PDB is no longer available, the standard carbonates now used are NBS 19 and 20.

1.5 Statistical Considerations

1.5.1 Mathematical Expression for Radiocarbon Age

The mathematical expression for the radiocarbon age of a sample is derived from the basic decay law $A(t) = A(0) e^{-\lambda t}$ where $A(0)$ represents the radiocarbon activity at point of death,

$A(t)$ represents the radiocarbon activity at time t after death and λ , the rate constant, is inversely proportional to the half-life of radiocarbon which will be denoted $t_{\frac{1}{2}}$. Arranging the radiocarbon age t to be the subject of the equation, this equation can be rewritten as

$$t = \frac{1}{\lambda} \log_e \frac{A(0)}{A(t)}$$

The radiocarbon age t is the desired item in dating and this means that estimates must be found for the parameters on the right hand side of the above equation. This leads us into the statistical domain.

1.5.2 Estimation of the Radiocarbon Age

Inserting appropriate parameters in the equation for the radiocarbon age we get

$$t = \frac{1}{\lambda} \log_e \frac{0.95 \theta_{ox}}{\theta_s}$$

where

$$\theta_{ox} = \text{true oxalic standard activity}$$

$$\theta_s = \text{true field sample activity}$$

$$\lambda = \frac{\log_e 2}{t_{\frac{1}{2}}}$$

Results are normally quoted in radiocarbon years before present (taken to be 1950 AD). It is also a convention that $t_{\frac{1}{2}}$ is taken to be 5568 years, the Libby half-life, rather than the more precisely measured half-life of 5730 years. The multiplicative factor of 0.95 is

to conform to the ^{14}C activity of the primary standard and so the overall term $0.95 \theta_{\text{ox}}$ represents the true modern activity. The normal practice in dating is for several oxalic acid samples to be used and a mean estimate of the true standard activity to be derived from those samples. Estimation of the true activity parameters pertaining to both oxalic and field samples is deferred until section 5 where a detailed approach to estimation of the radiocarbon age is considered.

The above statistical equation is just the Stuiver and Polach expression for age with A_{on} written as $0.95 \theta_{\text{ox}}$ and A_{sn} written as θ_s [46]. The choice to keep the multiplicative factor outside is arbitrary but useful inasmuch as the change from 0.95 to 0.7459 — i.e. the change from the oxalic I to the oxalic II standard — is more readily seen with this notation. It also homogenises the formulae for the normalised activities of both oxalic and field samples (see section 5.2). The Stuiver and Polach convention is virtually identical, however, and so no advantage is claimed for using a slightly different convention.

1.5.3 Signs of Statistical Progress

Improving the radiocarbon dating method is a sizable task encompassing all of the physico-chemical, experimental and statistical elements which constitute the entire process pertaining to the production of radiocarbon ages. The physico-chemical elements of the process are to be understood here as being the unseen atomic and subatomic events in the materials acquired for radiocarbon age evaluation. A better understanding of these events can only enhance the radiocarbon dating principle in general and would serve to reinforce the axioms of the principle.

Of the remaining two elements of the process, experimental and statistical, the statistical aspect is the one which this work focuses upon. They are not independent, however, and so it is important to examine the experimental aspect together with the statistical aspect. The experimental aspect is profoundly influenced by the particular laboratory processing the samples. This has been clearly and statistically demonstrated by an International Study Group (ISG) in a major inter-laboratory comparison [26]. In this study the ISG showed that for a series of eight replicate samples from one tree dated independently by twenty radiocarbon laboratories, systematic bias and unexplained variability were present among the ^{14}C data produced by the participating laboratories. The conclusion presented by the ISG at the end of that particular study was that the quoted errors of ^{14}C ages ought to be multiplied by a factor of at least 2 in order to provide a quoted error which accommodates variability existing across the different laboratories.

Another more recent inter-laboratory comparison has sought to quantify certain components of the variability observed in quoted ^{14}C ages and errors produced by different radiocarbon laboratories. The findings of this international collaborative study are presented in Radiocarbon, volume 32, number 3, 1990 which focuses on this particular study. The overview by Scott et al. [40] comments on a three-tier approach to the assessment of variability through three individual analyses of the counting, synthesis and pretreatment stages of the dating process. The conclusion presented in that overview was that the conclusion of the earlier ISG study concerning error multiplication is justified and that the quoted errors, although adequately reflecting internal laboratory variability in most cases, do not adequately reflect variability that exists across laboratories. Aitchison et al. [2] report that while only 3 out of 38 participating laboratories quote errors which significantly

underestimate their internal laboratory variability, 12 laboratories significantly underestimate external variability. Significant biases of quoted ages were also observed for 15 of the 38 laboratories and Baxter [8] reports that there was evidence of laboratory biases of between 50–250 years.

Quoted errors presented by radiocarbon laboratories are still therefore in need of modification in a substantial number of cases with some appropriate form of error multiplication required in those cases. Although the quoted error may need to be inflated in order to properly accommodate the external variability, it may need to be revised relative to internal considerations. In this present work the author seeks to refine the quoted error with a view to improving it by purely statistical means. That such improvement can be achieved is the motivation for this work and subsequent sections will show that better statistical management of ^{14}C data can reduce quoted errors, relative to internal considerations only, without dishonest manipulation of the data. It must be stressed that this is not a reduction of internal laboratory variability which is experimentally defined but of the quoted error which is statistically as well as experimentally defined. This point is extremely important. It must also be stressed that adoption of a refined quoted error without due consideration of error multiplication is not recommended by the author.

1.5.4 Sources of Error in ^{14}C Data

With a view to tackling selected statistical aspects relating to the quoted error — see particularly sections 5 and 6 — it would be of interest to briefly examine the primary sources of error in ^{14}C data with particular reference here to the liquid scintillation context.

The quoted error is clearly related to internal laboratory variability but is also related to the way in which the data is statistically managed and interpreted. Concerning the former relation, Polach [38] lists a considerable number of primary sources of error in ^{14}C data pertaining to the liquid scintillation process:

“Factors causing variation in count rates and performance by LS radiometry include: benzene contamination and/or quenching, photo- or chemi-luminescence, tritium (^3H), radon (^{222}Rn), foreign sources of ^{12}C , ^{13}C or ^{14}C , memory effects, benzene synthesis apparatus or counting vial or cap contamination, variation in count rate of ^{14}C -labeled and ^{14}C -free standards, C_6H_6 synthesis catalyst, isotopic fractionation during benzene synthesis, variation of ^{14}C detection efficiency and background count rate, equipment failure and cosmic and other radiations or external interference.”

This list provides a good reference for liquid scintillation laboratories to conduct internal checks with a view to diminishing the error contributions from these factors. Some different problems will be experienced by gas counting and accelerator mass spectrometric laboratories but the need for internal checking is universal in order to maximise internal laboratory efficiency.

It is commendable that some radiocarbon laboratories are not only prepared to conduct internal checks but also to report the findings of those checks. One example is the report published by Ede Hertelendi of the Debrecen Radiocarbon Laboratory [30] where gas contamination is cited as a primary source of error. Reports such as these are rewarding for everyone involved in carbon-14 dating.

1.5.5 The Quest for Quality Control

Clearly there needs to be an increase in quality control, both experimental and statistical, in order for radiocarbon dating to move forward as a whole. Suggestions for increased quality control have been put forward by several people. Long and Kalin encourage all laboratories to "demonstrate their adherence to a quality assurance program" [32], explaining that this program would provide continual internal checking for laboratories, this to be controlled by the laboratories themselves. The checking process would involve testing a number of samples known only to a limited number of laboratory personnel, these samples to be treated anonymously among regular samples, thereby providing a monitor for the laboratory. Switzur [52] also tackles some statistical aspects of quality control in his call for the use of statistical graphs in radiocarbon dating. These graphs plot the means and ranges (or standard deviations) of ^{14}C counting data with upper and lower action limits which encourage corrective action to be taken whenever counting data breach these limits.

The present work touches on two main aspects of statistical quality control. (Other aspects are considered and discussed but are not included in the software package which is the culmination of this work.) The first control is a means of continually monitoring for and dealing with anomalous data among ^{14}C counting data. The presence of aberrations in the data will unjustifiably inflate the quoted error unless corrective action is undertaken. A method is developed to make this corrective action statistically objective. The second control is a once-off refinement of the quoted error which is achieved through taking account of the correlation in normalised activities of oxalic standard and field samples.

The drive for increased quality control is an open-ended quest. The results of this work can only be a small contribution to such a large endeavour but hopefully a contribution

with a wider application than one laboratory. Since the work focuses exclusively upon statistical theory — no improvements in experimental practice are suggested by the author — the results here may have such an application. Certain idiosyncrasies pertaining to the Glasgow laboratory did, however, play a significant role in the development of the statistical methodology and thereby in the development of the software package which contains that methodology. The generability of the software is therefore of importance and is discussed in sections 7.1.2 and 7.2.2.

2 A Provisional Model for Background Activity

At the outset, some simple statistical studies were conducted on some background samples. These are the simplest samples to examine since the activities expressed by other kinds of samples — standard, field and spiked — are partially confounded with the background activity. This initial set of studies was carried out on all background samples produced in the Glasgow University radiocarbon dating laboratory over the period 3/6/80 to 31/10/80.

2.1 A Survey of the Background Data

Table 1 is a summary of the available background data for the relevant period. There are three source materials with respect to the produced background samples. These are :-

- (a) **calcium carbide** — this is a coal/oil derivative and as such contains no ^{14}C . It is usually supplied in the form of pellets and these pellets are converted to benzene via hydrolysis to acetylene and cyclotrimerisation.
- (b) **anthracite** — this is another form of ancient coal. Like calcium carbide it is inert with respect to radiocarbon.
- (c) **Scintillation Grade Benzene (SGB)** — this is produced commercially. The benzene is petroleum derived and contains no radiocarbon. As well as being used to produce background samples, it is also used to 'top up' samples whose benzene yields are less than the standard geometry weight (the optimal weight for the counting procedure).

The above three materials constitute the three main types of background test materials employed in radiocarbon dating. Recent attempts, however, have been made to extend

Background Data	Count
Source Materials	3
Background Samples	8
Batches	27
Samples (all occurrences)	94
Counting observations	918

Table 1: summary of available background data.

Sample Code	Source Material
B35	Calcium Carbide
B36	Calcium Carbide
B37	Anthracite
B38a	Calcium Carbide
B38b	Calcium Carbide
B39	SGB
B40	Anthracite
B41	Anthracite

Table 2: sample codes and their respective source materials.

the range of acceptable background test materials. Lowe [33] reports that preliminary investigations into the merits of geologically formed graphites as background test materials have proven favourable.

This work does not set out to prove one source material superior to another. The reliability of materials, and indeed of individual samples stemming from materials, would have to be ascertained in the light of the chemist’s working knowledge of the materials, with a knowledge of factors affecting the efficacy of the materials and all of this combined with the statistician’s skills in managing and interpreting data related to the materials.

The number of background samples available for study is 8 and their corresponding source materials are listed in Table 2. These samples appear in 27 batches over the time

interval being considered. The samples occur 94 times between them, not all concurrently, over the 27 batches. A total of 918 counting observations are amassed for all samples over all batches.

The distribution of samples and observations over the batches is recorded in Table 3. An examination of this table shows that there are five groups of batches with respect to concurrence of samples. These groups are specified in Table 4 with the longest group constituting 11 batches over which the same 4 background samples ran together. Another feature worth noting from Table 3 is that the standard number of observations is 10 per sample per batch. Where this has not been the case it is the result of a break in normal practice. The irregularity of batch 13, for instance, was the result of a fault in the refrigeration of samples for that batch.

The observations for samples in a batch form a time series. This is due to the cyclical method of measuring samples in a batch. This can be seen in the following definition:

Definition: a 'cycle' is a set of ^{14}C counting observations on all samples in a batch where the set contains only one observation from each sample and each observation shares the same index (1,2,3,...) according to its chronological position in the batch process. Measurements for one sample are not recorded in immediate succession of one another. Instead, all samples in a batch are placed in a circular conveyor system so that in one complete revolution of the process all samples are measured once — hence the name 'cycle'. The process continues until the desired number of cycles is attained. This means that observations, ignoring small variations in counting times, are generally equidistant time-wise and so form a genuine time series.

Sample	Batch Index																
Code	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
B35	10	10	10	10	10	10											
B36	10	10	10	10	10	10											
B37							9	9	9	10	10	10	3	10	10	10	11
B38a							10	10	9	10	10	10	6	10	10	10	11
B38b							10	10	9	10	10	10	6	10	10	10	11
B39							10	10	9	10	10	10	6	10	10	10	11
B40																	
B41																	

Sample Code	Batch Index										
	18	19	20	21	22	23	24	25	26	27	
B35											
B36											
B37			10	10	10	10	10	10			
B38a	10	10	10	10	10	10	10	10	10	10	
B38b											
B39	10	10	10	10	10	10	10	10	10	10	
B40	10	10	10	10	10	10	10	10	10	10	
B41									9	10	

Table 3: distribution of background samples and observations over batches.

Batch Group	Concurring Samples
1–6	B35,B36
7–17	B37,B38a,B38b,B39
18–19	B38a,B39,B40
20–25	B37,B38a,B39,B40
26–27	B38a,B39,B40,B41

Table 4: groups of batches with concurring samples.

Each batch accommodates only 10 cycles on average because of the data and program storage limitations of the Apple computer systems which are used in conjunction with the Packard counters. These limitations are now being resolved at the East Kilbride laboratory by the employment of more powerful IBM computer systems. Under the present system, radiocarbon ages of samples are not normally quoted until a series of about 6 batches containing the same samples have been processed — constituting an overall 60 cycle counting series — and the statistics from those batches are combined in some suitable manner. With the introduction of the more powerful computer system the data from batches may soon be aggregated and statistics derived directly from one large data set rather than from the pooling of the statistics from each of the smaller batches.

2.2 Preliminary Tests

Two preliminary tests are conducted at this stage of the study:

- It is of interest to test the hypothesis of no correlation among the background data. This hypothesis is presently assumed to be true in the estimation of the background activity.
- It is also of interest to test the hypothesis of the background data conforming to a normal distribution. This is also normally assumed to be true in the estimation of the background activity.

If either of these hypotheses is rejected, then the standard method of estimating the background activity is unsatisfactory.

The particular data tested are not the gross counts but rather the counting activities which, in the case of background samples only, are expressed simply in terms of counts per minute. These data will be referred to as the cpm values irrespective of the type of sample.

The data are assessed in these tests excluding 10 observations, i.e. only 908 observations were used. These 10 observations were considered to be outliers according to the rule of outlier detection developed and presented in section 3. This could justifiably be objected to on the ground that outliers may only be assessed as such in the light of the inherent structure of the data. For example, an outlier in data conforming to a skewed distribution would possess different characteristics to an outlier in data conforming to a normal distribution. This exclusion of 10 observations happened due to an unfortunate arrangement of priorities. The results derived from the trimmed set of 908 observations, however, will show that such an objection is largely academic here. The removal of a few observations has only served, in this case, to trim off a few ragged edges. It will become evident that their inclusion would not have reasonably altered the conclusions of the tests.

2.2.1 Testing the Correlation Hypothesis

It is of interest here to test the assumption of no correlation among the background data. Due to the plenitude of data, a portion of the data is chosen for the reason of parsimony. Whether this portion is truly representative of the whole data or not, is always a risk in sampling. Randomised selection would minimise this risk. The choice, however, is not based on randomisation but on qualitative and quantitative considerations with respect to the available background samples. Two samples are chosen for analysis, namely B38a and

B39, because they run together over 21 consecutive batches and because they represent two different materials — calcium carbide and SGB. Despite the non-random selection of these two samples, there is no reason, a priori, to believe that these two samples are uncharacteristic. Thus the conclusions derived from them will be considered to be of a general rather than sample-specific nature.

Before proceeding to test for significant correlation among the data, an assumption is made concerning this data. The assumption is that data pertaining to a single sample in a single batch possess stationarity with homogeneous variation. If the stationarity aspect of the assumption is not true, then it may be dealt with by differencing the data. If homogeneous variation is not true, then it may be dealt with by some suitable transformation of the data. A quick cross-sectional and graphical survey of the data, however, suggested that the proposed assumption is reasonable. This assumption is only provisional at best because of the small counting series of 10 cycles on average for each batch. A longer counting series for batches would allow a proper study of possible time trends and might generate an entirely different assumption. (A brief discussion of problems concerning time trends in counting data appears in section 5.4.)

The simple joining of batches here to form longer counting series is not performed — the observations from appended batches would not form time series in the strictest sense. The author recognises now that this may not matter too much if the batches are processed close to one another. This simply adds to the provisional nature of the conclusions pertaining to this particular study.

Due to the fact that each time series is very small — 10 observations are not going to yield powerful results — it is only possible to test the correlation hypothesis in a very

limited way. Two tests relating to correlation are performed here. The first examines for significant correlation in each batch between neighbouring observations within the two individual samples. The second examines for significant correlation in each batch between observations from the two different samples pertaining to the same cycle. The first test is equivalent to an auto-correlation test of lag 1 for each sample in each batch and the second test is equivalent to a cross-correlation test of lag 0 between the two samples in each batch.

The auto-correlation test is applied first. If one sample in one batch produces a significant result, then this result will be weak in the light of the small sample size. If, however, over all batch-sample tests we find a considerable number of significant results, then evidence of non-spurious correlation among the data is stronger.

The significance of a single batch-sample test is straightforward. We simply construct a 95% confidence interval for the hypothesis of zero correlation and test to see if the result lies outside of this. There are a total of 42 batch-sample tests — 2 samples over 21 batches. It is of interest to see what proportion of these tests are significant. Given that 5% of the tests on average should prove significant by chance, presuming the hypothesis of zero correlation to be true, then any observed percentage greatly in departure from 5% will be interpreted as evidence of non-spurious correlation.

For a time series process X_t , the auto-correlation function (ACF) with lag 1 is defined as

$$\text{ACF}(1) = \frac{\text{Cov}(X_t, X_{t+1})}{\text{Var}(X_t)}$$

Given a realisation of the X_t process, that is, a finite time series of n observations

x_1, x_2, \dots, x_n , $\text{ACF}(1)$ is estimated from the formula

$$\text{ACF}(1) = \frac{\sum_{t=1}^{n-1} (x_t - \bar{x})(x_{t+1} - \bar{x})}{\sum_{t=1}^n (x_t - \bar{x})^2} \times \frac{n}{n-1}$$

The standard error of $\text{ACF}(1)$ is given simply by

$$\text{SE}[\text{ACF}(1)] = \sqrt{1/n}$$

A result is considered to be significant if the ACF value lies outside of $\pm 2\text{SE}$. The ACF values are plotted in Figure 1 and are standardised by dividing by 2SE — this means that any value which has an absolute value greater than 1 is statistically significant. From the plot it can be seen that only 2 out of the 42 batch-sample tests are significant. This is near enough 5% and so it is entirely agreeable with chance. The conclusion therefore is that there is no real evidence from this data that neighbouring background measurements are correlated. The possibility of significant correlation being present beyond lag 1 is remote in the light of this conclusion.

It remains now to check for simple correlation between data across the background samples in each batch. The cross-correlation function (CCF) with lag 0 is estimated using the following formula where we are dealing with the realisations of two coincident time series processes X_t and Z_t :

$$\text{CCF}(0) = \frac{\sum_{t=1}^n (x_t - \bar{x})(z_t - \bar{z})}{\sqrt{\sum_{t=1}^n (x_t - \bar{x})^2 \sum_{t=1}^n (z_t - \bar{z})^2}}$$

The standard error for the CCF function is given by

Figure 1 : standardised acf values for samples B38a and B39

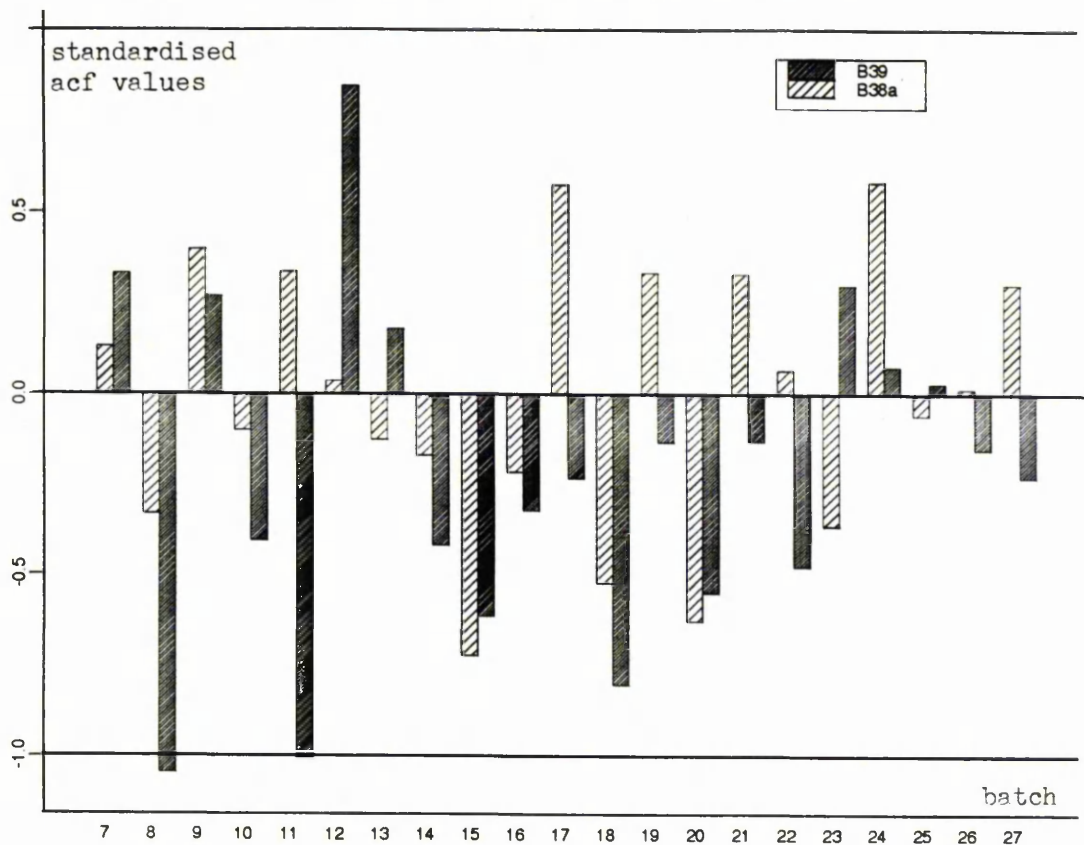
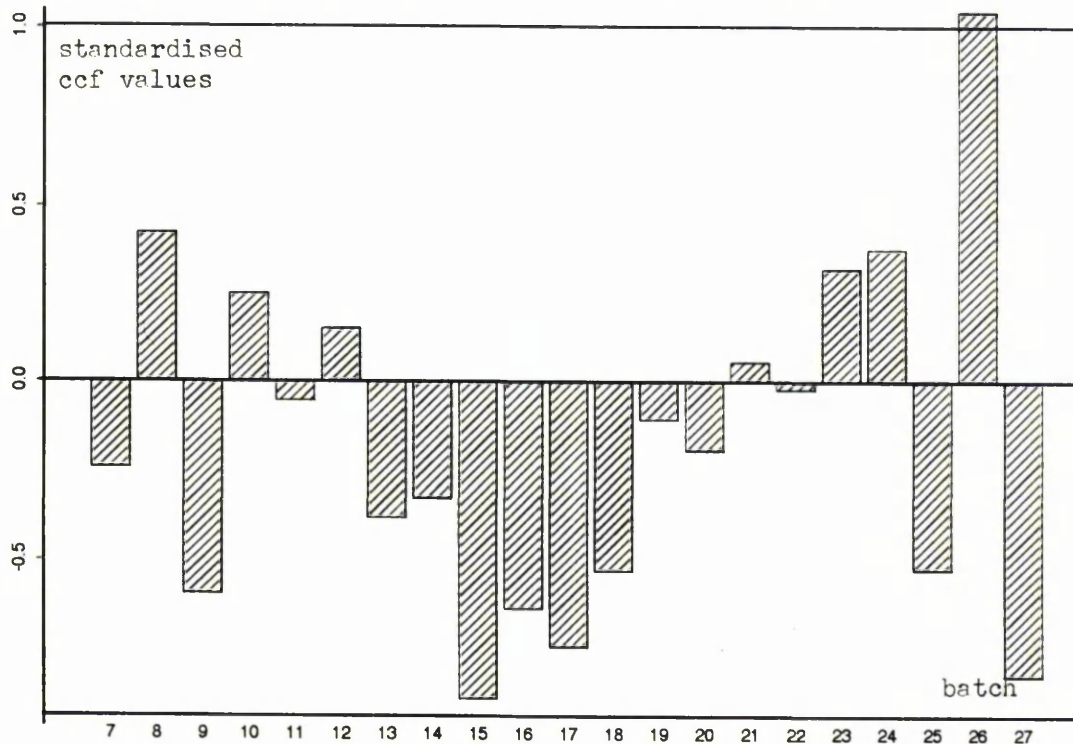


Figure 2 : standardised ccf values for samples B38a and B39



$$\text{SE}[\text{CCF}(0)] = \sqrt{1/n}$$

The CCF values for samples B38a and B39b over the 21 batches are standardised in the same manner as the ACFs and plotted in Figure 2. The CCF plot is consistent with the ACF plot in that only 1 out of 21 tests is significant which is once again agreeable with chance. The conclusion is that data belonging to different background samples within a batch are not correlated.

The results from both the auto-correlation and cross-correlation studies allow an informal statement of two assumptions normally held to be true in the estimation of the background activity:

(A2.1) Observations within background samples in a batch are uncorrelated.

(A2.2) Observations across background samples in a batch are uncorrelated.

The above assumptions are confirmed for this data at least. The extension of these assumptions to longer counting series and/or to data produced by other laboratories is not automatic. This requires caution. The conclusions here only provide a provisional model for the background activity which may need to be modified in a different context.

2.2.2 Testing of Normality Hypothesis

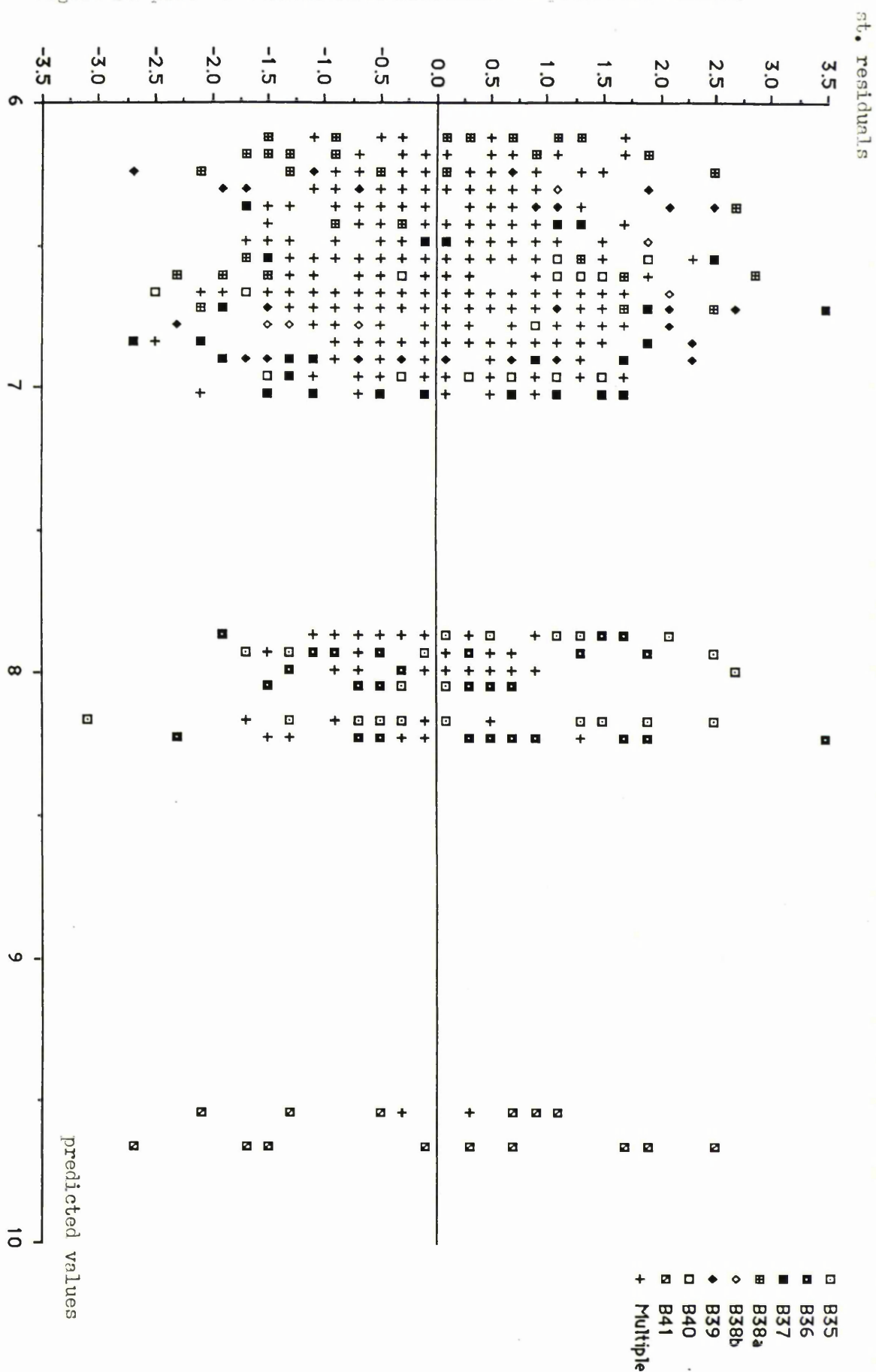
To test the assumption of normality pertaining to background data, a simple fixed effects model is proposed for and fitted to this data. The fact that it may be an over-simplified model is not too important here. The model is a standard two-way classification:

$$y_{jkl} = \beta_j + \gamma_k + \epsilon_{jkl} \begin{cases} j = 1, \dots, J \\ k = 1, \dots, K \\ l = 1, \dots, L_{jk} \end{cases}$$

where β_j denotes the j th sample (material is subsumed in this term), γ_k denotes the k th batch and ϵ_{jkl} is a random error component arising from a normal distribution with mean 0 and variance σ^2 .

Figure 1 shows a plot of standardised residuals against predicted values of the data with each sample denoted by a different symbol. There is no unusual pattern here that would suggest non-normality. Of the 908 observations, 41 produce standardised residuals with values greater than 2.0. If we take into account the 10 observations that were excluded, then 4.5%–5.6% of the observations lie in this range. This conforms agreeably with chance among data that are normally distributed. There is also no evidence of heterogeneous variation among the standardised residuals and the picture is what would be expected given an assumption of normality. Figure 2 is a plot of standardised residuals against normal scores (the expected order statistics for a normal distribution with zero mean and unit variance). The linear pattern shows that the assumption of normality is good.

Figure 3: plot of standardised residuals v. predicted values.



3 Screening for Outliers

One of the points of interest in this study is to see if some method can be established to identify and suitably deal with outliers. The term 'outlier' is used in this context to mean an observation that is unrepresentative of the underlying process that is being examined, this characteristic being demonstrated in the observation being significantly different from the main bulk of other observations corresponding to the same process. Expressing this another way, an outlier is a datum which possesses some properties(property) that set(s) it ostensibly and measurably apart from the rest of the data.

To cite an example, an observer may be very surprised to find a recording of 6' 2" among the heights of children attending the first year of some primary school. This would no doubt invoke extreme scepticism on the part of the observer. The initial reaction of the observer might be to assume that a recording error has been incurred by the teacher and that the figure of '6' really ought to be a '2' or a '3' at most. What is more important, however, is how this particular datum is treated. If, for example, the observer is required to evaluate a class average of the childrens' heights, the important issue is one of the treatment of the data rather than an explanation of the anomalous datum which may or may not be legitimate (although an explanation is obviously useful and desirable if such can be found). Even if the observation should turn out to be legitimate, the question comes down to that of its representativeness.

Thus it is necessary to consider what should be done with the maverick observation. If the observation is included, then it may give a false impression of the general height of the children in the particular class, possibly leading to the erroneous conclusion that this class is occupied by a genetically peculiar breed of children. The observation may be

dropped, on the other hand, since it might be considered to be completely (or at least highly) unrepresentative of the general height of the children. Yet again, some central measure of height may be employed which attaches less emphasis to the more extreme recordings of height than would a simple class average. Such a measure could be the class median. Whatever course of action is taken, it is possible, in this case, that curiosity might prompt the observer to contact the school in order to determine if the eccentric datum is real or not.

This hypothetical case is not an entirely implausible one — teenagers with serious learning difficulties have been known to occupy primary school classrooms. The above principles of treating an outlier, however, may now be applied to the case at hand, namely the radio-carbon study. An option that cannot be entertained here is to go back to the experiment and validate or invalidate the results. Once a measurement has been recorded it is not reproducible but is entirely local to its time of recording. Thus the data stand unalterable unless it is clear that an error has been made and the exact nature of that error is known. Thus it will be of secondary interest to explain anomalies in the data since precise explanations for errors will seldom be available. The primary interest will be of objectively defining outliers and then suitably dealing with them.

The practice till now has been to make subjective judgements about the data and to simply reject observations which appear to seriously 'stick out'. What is sought here is to make the judgement procedure a more objective one by using statistical methodology. The practice of data rejection, however, will be retained. This is the simplest course of action to take short of simply retaining the data. This latter course of action, without any adjustments to the data of any kind, is undesirable since significantly deviant count rates

would not generally be perceived as data belonging to the main underlying process. (They may in fact be extremes of that process and thus belong to it but are too extreme to consider inclusion in subsequent calculations applied to the data.)

An alternative option might be to retain the outliers and at the same time reduce their influence by using robust measures of central location such as the sample median. This treatment is generally referred to as *outlier accommodation*. The problem with this option, however, is that it would be difficult to combine robust measures from several samples and several batches if such are to be favoured over the simpler sample means. By simply dropping 'corrupt' data, it is possible to proceed with the sample means which can be then be suitably combined and an estimate of error produced with relative ease. Distributional properties of means and linear combinations of them are more mathematically tractable when the underlying process is normal.

With an aim to rejecting outliers, it is now only required to develop some adequate means of detecting them. Before doing this, however, it is useful to look briefly at some existing methods of treating outliers.

3.1 A Brief History of Outlier Detection

Early methods of treating outliers were essentially unsophisticated as one might expect. Barnett and Lewis [7] make the following comment in the preface of their comprehensive publication on outliers:

"The early emphasis stressed the contamination of the data by unanticipated and unwelcome errors or mistakes affecting some of the observations. Attitudes varied from one extreme to another, from the view that we should never sully the

sanctity of the data by daring to adjudge its propriety, to an ultimate pragmatism expressing 'if in doubt, throw it out'."

Both of these approaches are wholly crude by modern standards and would certainly be considered unworthy today (which is not to say that they are still no longer practised). The former approach is snobbish and inflexible, giving the data even greater authority than the analyst. This might please certain people who do not trust in the integrity of analysts but it makes unsubstantiated claims about the integrity of the data. The latter approach is far too vague and subjective. It could give vent, consciously or unconsciously, to a 'mould the data to fit the preconceptions' approach to data analysis. Thus neither approach is satisfactory.

Two early and important attempts at an objective approach to the identification of outliers are worth mentioning here. The first was a method proposed by Chauvenet [13] in 1866. Chauvenet defined an outlier to be any observation in a sample whose deviation from the sample mean is such that the probability of a deviation as large or larger is less than $0.5/n$. The problem with this approach is that it rejects, on average, half an observation of good data in any sample no matter what the sample size is. Two years later Stone [43] took a different approach by assuming that an error in the recording of data will occur with some frequency $1/m$. An outlier is now any observation whose deviation from the sample mean is such that the probability of a deviation as large or larger is less than $0.5/m$. This appears at first sight to be Chauvenet's method dressed up in a different notation but they are quite dissimilar since here a fixed proportion of good data in a sample are rejected and the number of outliers increases with the sample size.

More recent approaches to the treatment of outliers have naturally taken on a greater sophistication. This is because the treatment of outliers, in recent years, has become a

respected statistical discipline in itself and not just some appendage to other statistical disciplines. For the purpose of clarity it is useful to divide the treatments into two general categories :-

- Those which accommodate outliers. No outlier description nor detection is essential in these treatments and outliers are retained in the data although their influence is diminished by use of robust methods.
- Those which seek to define and identify outliers among the data and then remove them on discovery. The principle of outlier detection and subsequent rejection is the one adopted in this study.

The first category of outlier treatment is an indirect approach and, as such, does not compel the analyst to provide a formal definition of outliers though one may be supplied. The influence of outliers is simply diminished by attaching less importance to the extremes of the data. In these methods we find sample means being pushed aside in favour of more robust estimators of central location, viz. (1) L estimators (estimators based on order statistics), (2) M estimators (estimators based on residuals and moments) and (3) Bayesian estimators. These statistics attach less weight to the extremes of the data. A comprehensive account of these statistics is provided by Huber [31] and, more recently, a useful and brief general review is provided in the paper by Beckman and Cook [9].

The outlier accommodation approach does not really require observations to be identified as outliers because it seeks only to weight observations relative to their distance from some common centre without ever rejecting them. Statistics other than the ordinary sample means, however, tend, in the case of a Gaussian process, to be less tractable with respect

to distributional properties. This difficulty is further compounded when several groups of data are required to be analysed and estimates from each combined in some appropriate manner. For instance, in combining several sample medians from different groups of data it is a fact that the median of the medians is not identical to the median of all the data put together. Sample means, on the other hand, may be straightforwardly combined as long as the number of observations that make up each mean is known. For these reasons, and on account of the general simplicity of sample means, the option of outlier accommodation is not adopted in this study.

The second category of outlier treatment involves the definition and identification of outliers using suitable statistical means and the subsequent removal of those outliers from the data. The removal of outliers from the data allows the analyst to safely work with the sample means assuming that the samples are free from more global kinds of contamination. This makes further analysis considerably easier.

Let us therefore consider this latter category of outlier treatment. This treatment requires a formal definition of the outlier. Most methods of outlier detection adopt a common sense approach although the formalisation of tests relating to these methods goes a lot further than common sense. What is meant by a common sense approach is that most of the methods are intuitive in their choice of test statistics. For example, let us suppose that it is desired to conduct a test for a single outlier in a normal sample with mean μ and error σ . Suitable test statistics for this situation could be the residuals $|X_{(i)} - \mu|/\sigma$ and the test would be to reject any observation X_i whose residual was unduly large. In practice, μ and σ would be replaced by sample estimates. The value of μ could be taken to be any measure of the central location such as the sample mean, sample median or any other exotic measure of

central location. The value of σ may be taken to be any measure of dispersion such as the sample standard deviation or the sample range. If the sample mean and sample standard deviation are chosen and the biggest residual is tested, then this case is well documented [35, 27]. In that particular test the observation with the largest residual would be removed if its value was larger than some estimated percentage point of its null distribution. This test could be applied recursively so that the largest residual of the reduced sample could then be tested and so on. Recursive detection of a single outlier, however, has been noted by Pearson and Chandra Sekar [35] as being ineffective due to the problem of masking, namely, that if two or more outliers are present in a sample, then successful detection of an outlier is somewhat hampered by the eclipsing effect of the other outliers present in the sample.

The problem of masking has encouraged the development of outlier detection methods which seek to identify clusters of outliers in data samples and to remove any detected cluster rather than remove outliers one at a time. Several multiple outlier detection methods exist and it would be useful to mention a few such methods here. A broader and more detailed survey of these methods may be found in the statistical monograph by Hawkins [29]. One commonly used multiple outlier detection method — modified versions also exist — is one which is proposed by Tietjen and Moore [53]. The proposal is to test for k outliers using the statistics

$$E_k = \frac{\sum_{i=1}^{n-k} (Z_{(i)} - \bar{Z}_{n-k})^2}{\sum_{i=1}^{n-k} (Z_{(i)} - \bar{Z})^2}$$

where $Z_{(i)}$ are the order statistics of the observations $Z_j = |X_j - \bar{X}|$, $j = 1, 2, \dots, n$ and $\bar{Z}_{n-k} = \sum_{i=1}^{n-k} Z_{(i)} / (n - k)$ with $k \leq [n/2]$. Another approach is one adopted by Tiku [54] using the statistic

$$T(r_1, r_2) = \frac{h\tilde{\sigma}_c}{\tilde{\sigma}}, \quad h = \frac{E(\tilde{\sigma})}{E(\tilde{\sigma}_c)}$$

where $\tilde{\sigma}_c$ is the ML estimator of σ calculated from the type II censored sample

$$X_{(r_1+1)}, X_{(r_1+2)}, \dots, X_{(n-r_2)}$$

and $\tilde{\sigma}$ is the ML estimator of σ calculated from the complete sample.

A more recent attempt at multiple outlier detection has been a graphical method employed by Bacon-Shone and Fung [6]. In this method the test statistic used, in the multivariate case, is the ratio of the determinant of the scatter matrix with a certain number of observations removed over the determinant of the scatter matrix with all observations (substitute simple variance sums of squares in the univariate case). This statistic, called $R_{(t)}$, has known distribution for normally distributed data courtesy of Wilks [55]. One drawback is that it does not specify the number of outliers in a data set but the authors overcome this by the use of a graphical technique in which the observed $R_{(t)}$'s — a logarithmic function of them to be precise — are ordered and plotted against the expected quantiles. The plot should be approximately linear in the absence of outliers.

3.2 Outlier Detection Using a Simulation Approach

The procedure of outlier detection adopted in this study relies on a simulation approach. The efficacy of the method is ascertained according to its simplicity and its fundamental ability to suitably identify outliers.

Methods which do not anticipate outliers in the data are of no practical use here. This would exclude methods such as the Bacon-Shone and Kung method since a data plot is required to be analysed after each new data set is treated using that method. What is

required here is a fully automatic method of detecting outliers which can be used to reject corrupt observations from the unseen data. This means that the system must anticipate outliers in the data and therefore must not be an exclusively post-data method. This means that the data must have certain consistent features which allow such anticipation. Fortunately, these features are present in the data.

Two outlier situations are addressed in this particular study, namely a single outlier and an upper and lower outlier-pair. The need for a more extensive method of outlier detection (detection of three or more outliers) would be rather over-elaborate for this present data. With the size of the counting series of a single batch being around 10 cycles on average, multiple outlier detection would be a bit like using a mallet on a drawing pin. However, if the samples should be larger than 10 cycles, which will happen if the data from batches are to be aggregated in the future at East Kilbride, then a more extensive method would be required. This point is reviewed again later in the report.

The approach taken also uses outlier detection statistics which do not require tables of (estimated) percentage points to be written into the software. This could become tedious and inconvenient if the tables are required to accomodate a large number of (estimated) percentage points. Of course, the relevant statistics could be pumped out and checked by hand but this defeats the intention of a fully automated system. What is ideally required, then, is a self-contained method of detecting outliers which identifies anomalous data and deals with them directly without the system or system operator having to look up tables.

3.2.1 Statistics Employed in Detection

The method is a simple one that employs two statistics which are used to ascertain the presence of outliers in data. The two statistics used in this capacity can be expressed as

$$\begin{aligned} Z &= \frac{\max_i |X_{(i)} - M|}{G^*} \\ W &= \frac{X_{(n)} - X_{(1)}}{G^*} \end{aligned} \tag{10.1}$$

where $X_{(i)}$ is the i th order statistic, M is the median and G^* is a robust estimator of dispersion which will be defined shortly. These statistics are clearly related to one another but have different purposes. The Z statistic is useful for detecting a single upper or lower outlier. It simply represents the largest standardised departure from the median incurred by an observation among some unseen sample. The W statistic is the standardised range of the unseen sample and is useful for checking the presence of an upper and lower outlier-pair. Some work on this latter kind of test for an outlier-pair has been done by Pearson and Hartley [36] where the studentised range was used instead of G^* .

The need for both Z and W may seem superfluous but W ought to be more sensitive to an outlier-pair by its very definition than Z . For instance, it may be possible that two extreme observations belonging to some data sample may be significantly far apart with respect to a particular percentage point of W while individually neither observation is significantly far apart from the sample median with respect to the corresponding percentage point of Z . In practice, the situation of an upper and lower outlier-pair did not occur and so the usefulness of employing W as well as Z cannot be sufficiently assessed here. It is worthwhile, nonetheless, retaining both statistics even if this should be duplication because there is no harm in using both. (The computer gets to do the extra work at any rate.)

The choice of the median is entirely arbitrary. It provides no greater usefulness than any other measure of the central location. Its property of robustness lends it no greater advantage over the mean because the nature of the simulation method is that it works with any measure of central location with equal ease. The measure of dispersion G^* is defined as

$$G^* = \frac{2}{n(n-1)} \sum_{i=1}^{n-1} i(n-i)(X_{(i+1)} - X_{(i)}) \quad (1.1)$$

The choice of this estimator was again an arbitrary one since the method does not rely on the particular choice of the estimator of dispersion. It might seem a little overdone to use an estimator of dispersion that isn't particularly obvious or conventional (it was derived during a time of considering robust estimators). Nonetheless, the G^* statistic has certain properties which are worth noting and which make it a reasonable choice of estimator. For a start, it is simply a variant of Downtown's estimator except for a multiplicative constant. This latter estimator is

$$" \sigma " = \frac{2\pi}{n(n-1)} \sum_{i=1}^n [i - \frac{1}{2}(n+1)]X_{(i)}$$

The proof for the correspondence between G^* and " σ " is provided in the proof at the end of the section.

David [19] points out that " σ " is a highly efficient and unbiased estimator of the true population error σ and is not as influenced by the presence of outliers as are many other estimators such as the standard error and the range. This estimator is itself just a variant of Gini's mean difference, namely

$$G = \frac{1}{n(n-1)} \sum_{i,j=1}^n |X_i - X_j|$$

Thus the G^* statistic has a good pedigree belonging to a family of estimators which are known to be highly efficient. The form of the G^* statistic also makes it a little clearer than its variants how it works as an estimator. From the definition of G^* , it can be seen to be a linear combination of the differences between consecutive order statistics, each difference being given a particular weight. Greater weight is given to the more central observations and less weight is attached to the more extreme observations and so it can be seen that G^* is inevitably going to be relatively insensitive to the presence of outliers.

3.2.2 Standardised Statistics

An important assumption concerning both Z and W is that they are both standardised statistics, i.e. the mean and variance of a sample of data stemming from a normally distributed population will have no bearing on the percentage points of Z and W for any particular sample size. This assumption is not established theoretically here due to the relative complexity of the G^* statistic. Since the median, however, under the assumption of normality is an unbiased estimator of the true population mean and since G^* is a variant of Downtown's estimator except for a multiplicative constant — this latter estimator being a known estimator of the true population error — then it is reasonable to make the given assumption. To be on the safe side, however, a straightforward simulation is conducted to confirm the assumption as correct.

Data are generated for three independent normal distributions covering a limited range of data corresponding to low count sample activities (cpm/g). The means and errors of the

three normal distributions employed are (errors are based on Poisson counting errors for simplicity) :-

$$\left. \begin{array}{ll} \mu = 5 & \sigma^2 = 0.125 \\ \mu = 7.5 & \sigma^2 = 0.1875 \\ \mu = 10 & \sigma^2 = 0.250 \end{array} \right\}$$

For each of these distributions, 1000 samples each comprising 10 observations are generated. The choice of sample size 10 is to reflect the standard laboratory practice. These data are generated using a Gaussian random number generator provided among the standard Fortran library routines. For each sample the Z and W values are evaluated and then the values are ordered for each of the three distributions. The cumulative frequency plots for both Z and W are shown respectively in Figures 5 and 6. These plots reveal quite clearly that Z and W are not dependent on μ and σ . A formal test is not really required since the plots are satisfactory evidence in themselves and serve to confirm the assumption of standardisation.

3.2.3 The Automatic Detection Method

The final step in obtaining the complete method is to show that the sample size is conveniently related to at least one suitable estimated percentage point of both the Z and W distributions. (An approximation of the percentage point is derived via simulation for both Z and W .) To show this, it is necessary to decide what the typical range of sample sizes is. An examination of the data in Table 3 (see section 2.1) suggests that sample sizes from 4 to 12 should be considered. Sample sizes of less than 4 are unworthy of consideration and sample sizes greater than 12 are highly improbable due to the nature of the running checks

Figure 5: cumulative frequency plots for the Z-statistic

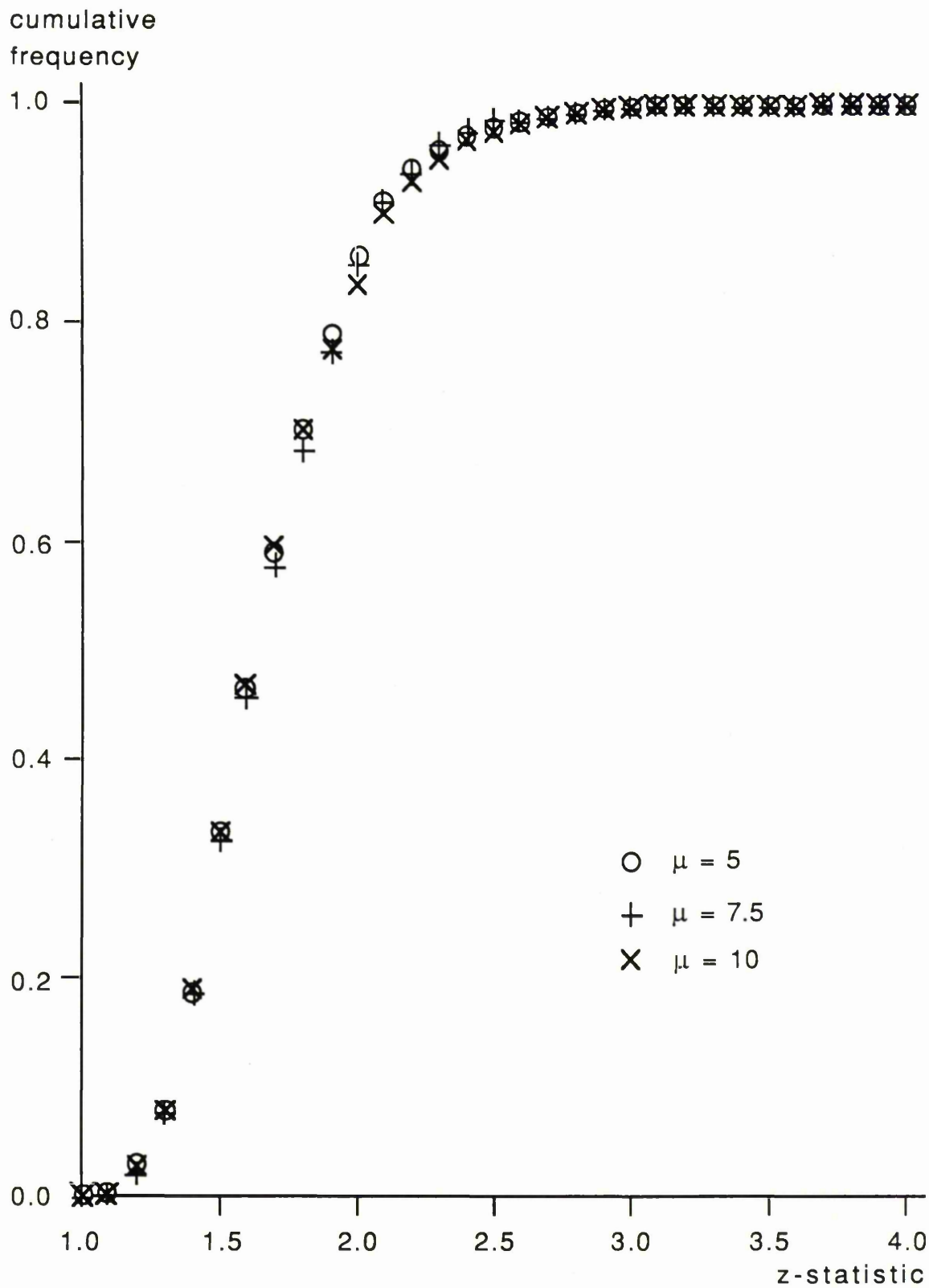
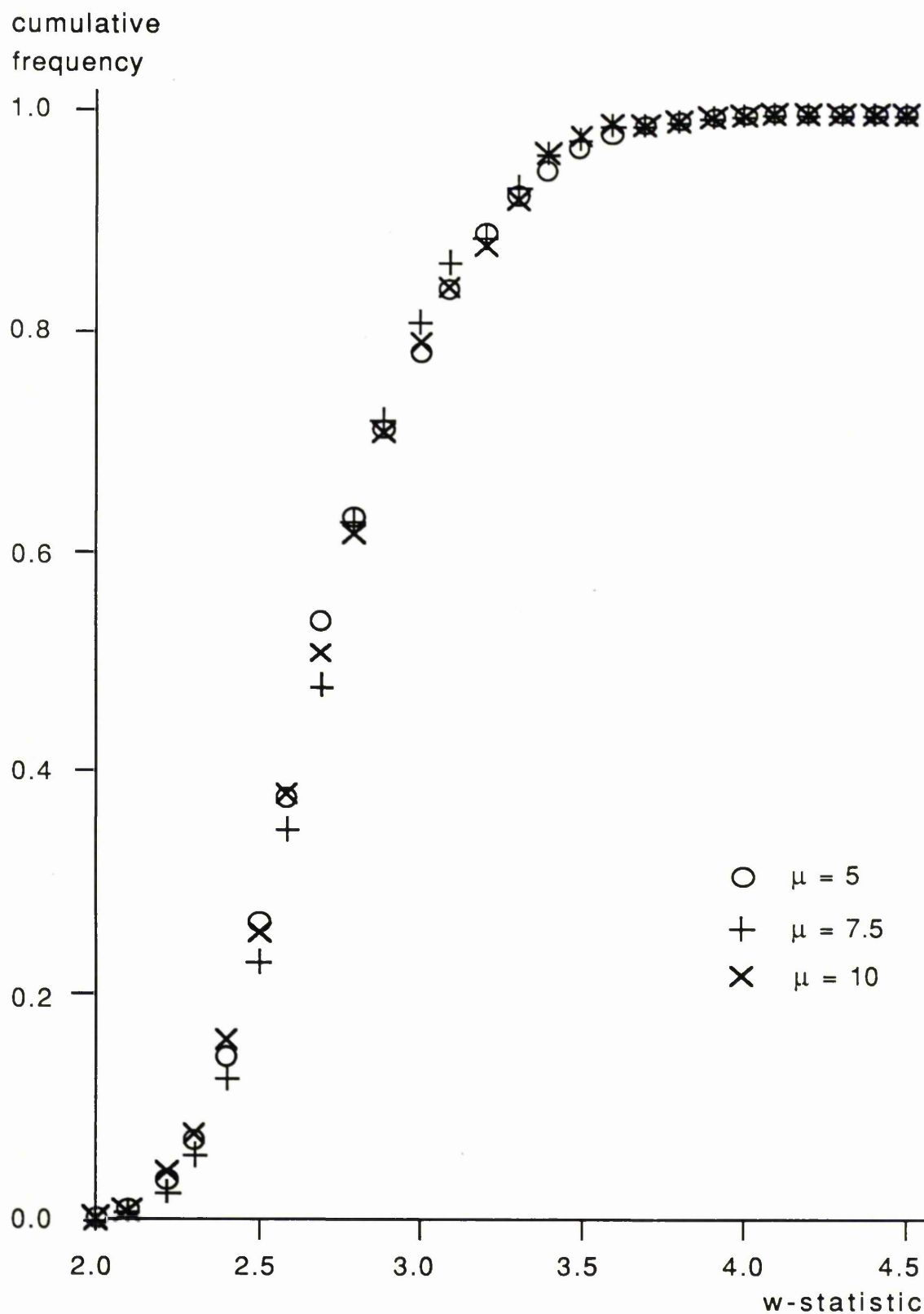


Figure 6: cumulative frequency plots for the W-statistic

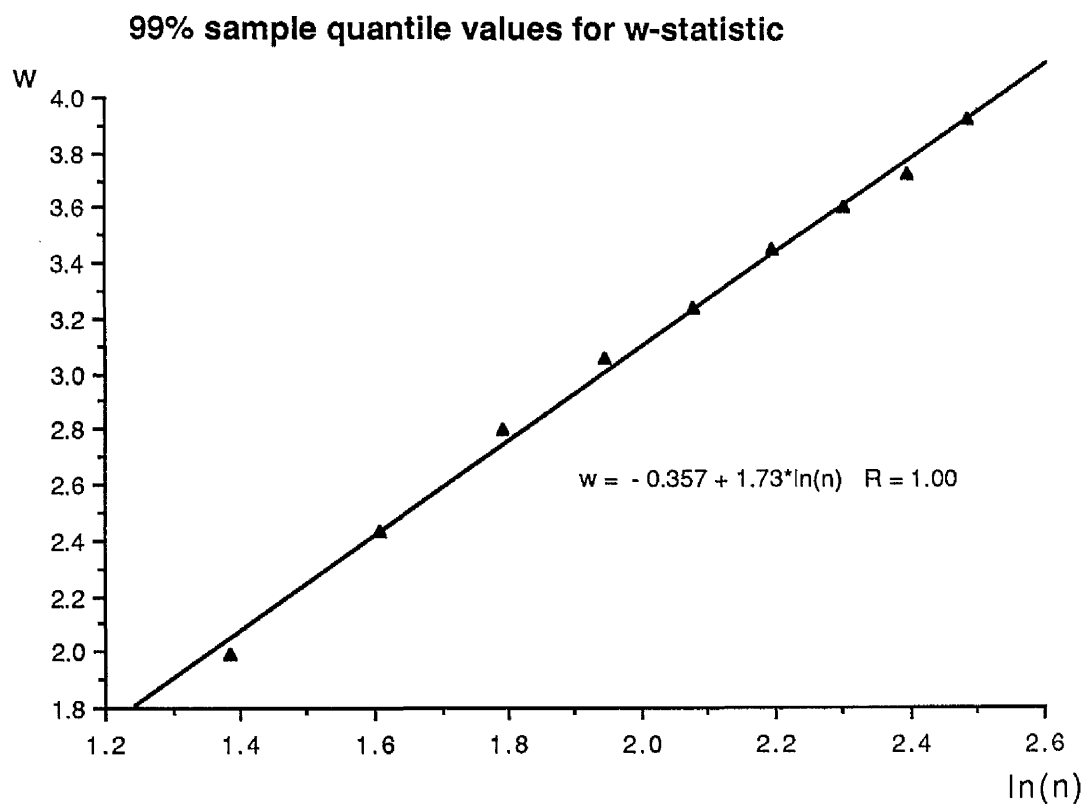
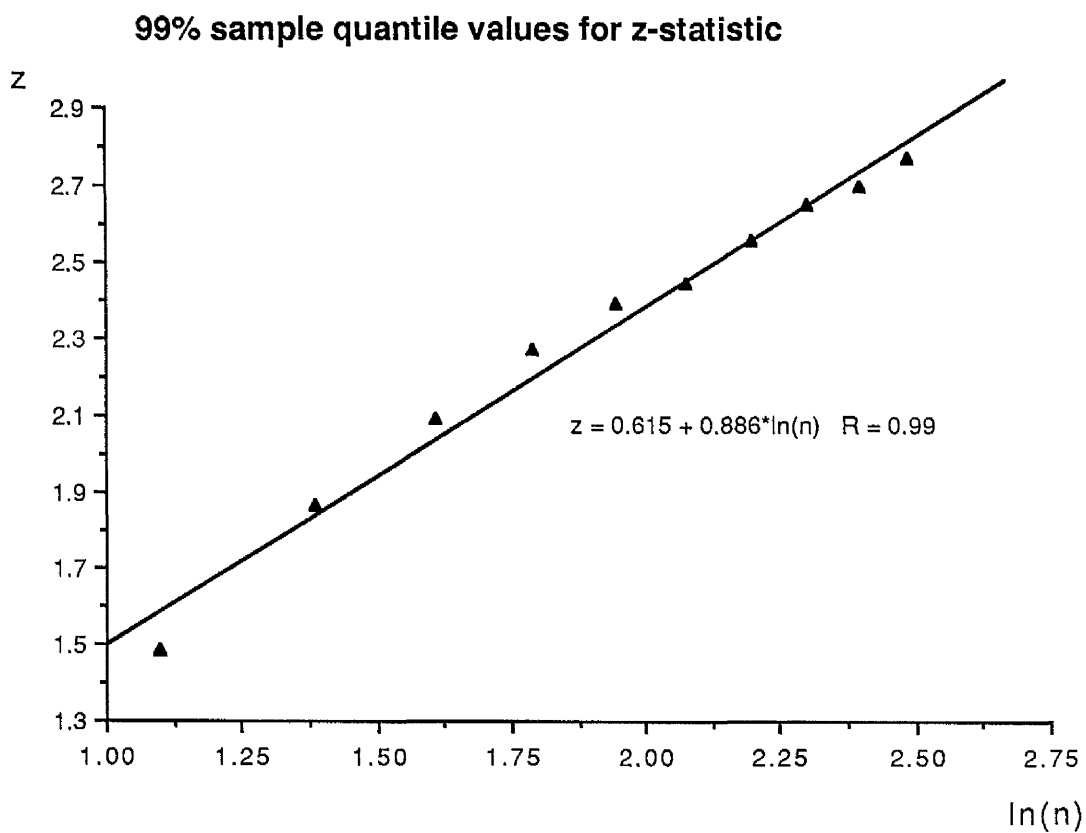


on samples which requires batches to be relatively small.

For each individual sample size, 1000 samples are generated from Gaussian data. Subsequently, the 99% quantile values (i.e. the sample approximations of the appropriate percentage point) are evaluated for both Z and W over all sample sizes. These quantile values are plotted against the natural logarithm of the various sample sizes in Figure 7. The choice of 99% is a conservative one but this ensures that approximately only one batch out of every 100 batches is likely on average to produce Z and W values in excess of the quantile value for the particular sample size as a consequence of mere chance rather than as a consequence of genuine data contamination. Given that a typical batch will involve processing around 20 samples of various sorts, this ensures a reasonably low probability of coming across a genuinely outlier-free or clean batch with a significant Z or W value among its samples. A choice of 95% is not commendable since at least one batch on average would be expected to be 'naturally' significant with respect to both Z and W .

From the plots it can be seen that the quantile values of Z and W are approximately linearly related to the natural logarithms of sample sizes. The regressions appear to be good with little variation of observations around the fitted lines although there still appears to be a slight non-linear trend, particularly in the case of the Z statistic. However, the correlation coefficients of 0.99 and 1.00, respectively, for the Z and W statistics show that the linear regressions are essentially adequate. This simulation study has therefore produced the following rule for determining the presence of outliers in a sample of $4 \leq n \leq 12$ normally distributed observations:

Figure 7: regressions of 99% quantiles on logarithms of sample sizes



(n = no. of observations)

A sample contains anomalous datum or data if

$$\left. \begin{array}{l} z \geq 0.615 + 0.886 * \log_e n \\ \text{or } w \geq -0.357 + 1.73 * \log_e n \end{array} \right\} \quad (\text{E3.3})$$

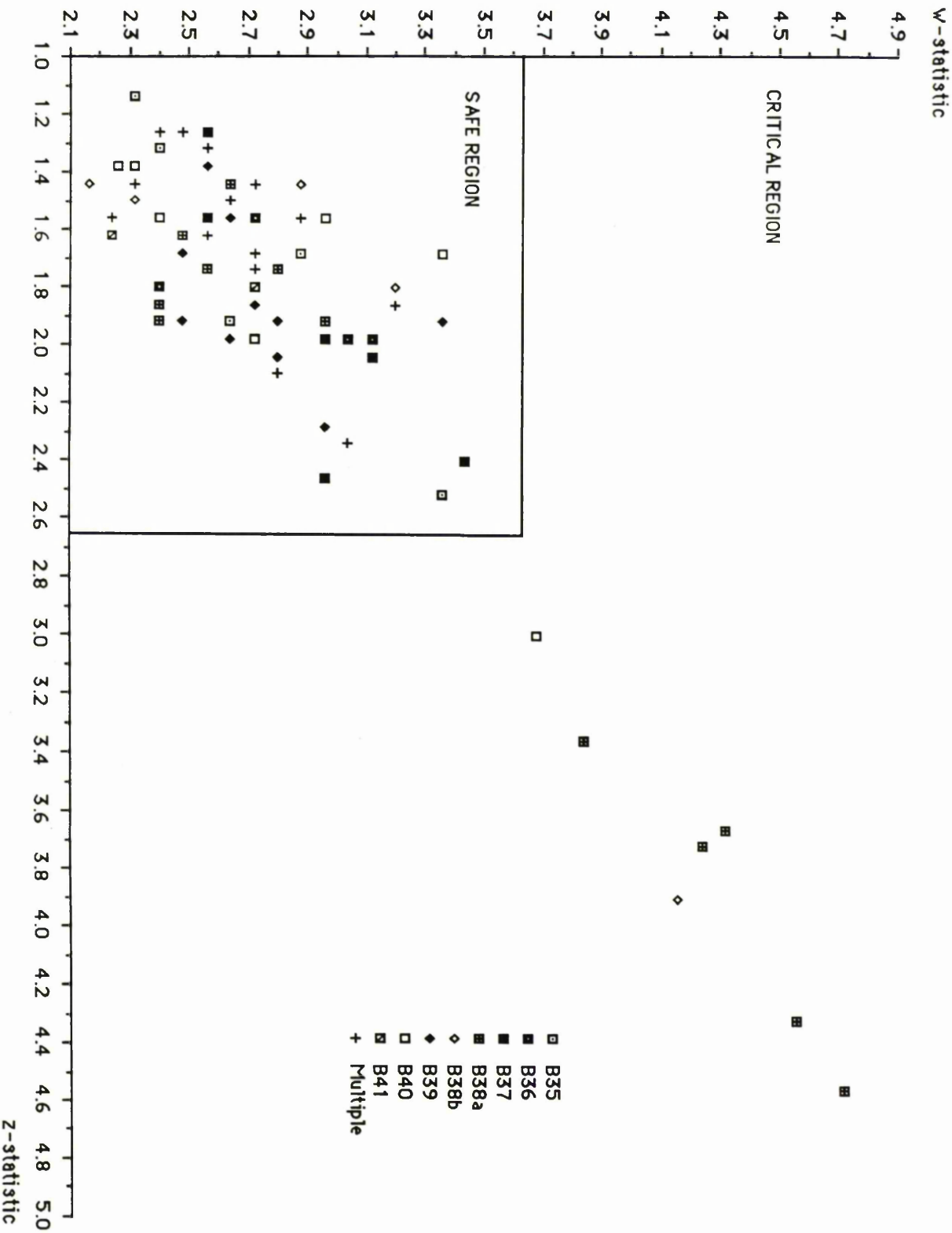
This simple method avoids the need for working with tables of any kind and provides a suitable degree of objectivity in the assessment of sample contamination. It can be seen, however, that it is only an approximate method since it does not use exact percentage points. The use of sample quantiles and the regression of those quantiles on the the natural logarithms of sample sizes makes for a double approximation but it is hoped that the approximation is a good one due to the large number of data sets used to derive the quantiles for both Z and W and the good fits produced by the regressions. (It may be argued that the double approximation could have been avoided by using established test statistics with available (estimated) percentage points rather than concocting new test statistics. This argument is accepted by the author but the idea of regression was not thought of until Z and W had been fully developed and it is not known what regression applied to the (estimated) percentage points of other more traditional test statistics would result in.)

3.3 Application of Detection Method

The method must now be examined in the light of its application to data. The first step taken here is to take all background samples of sample size 10 over the relevant period of time. This constitutes 79 samples. These are processed and Z and W values are determined for all samples.

The results of this study are presented in Figure 8. The critical values of Z and W are

Figure 8: Z and W statistics for all background samples of size 10



marked out by perpendicular lines through each axis. These critical values conform to the rule given in equation (E3.3). The perpendicular lines mark out a safe region and a critical region. The results show that 7 out of 79 samples are clearly contaminated.

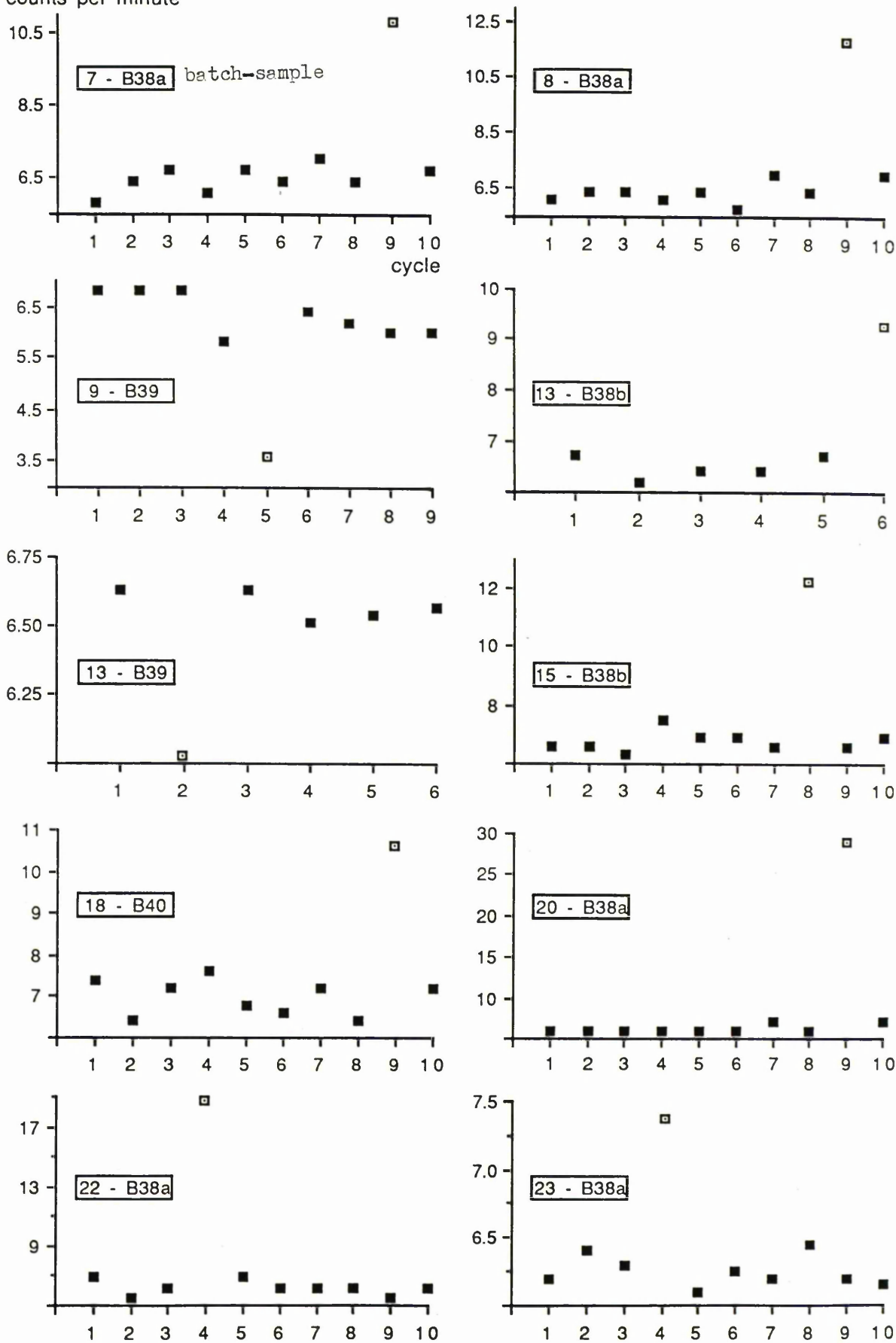
Other features to note are the close relationship between Z and W and that whenever Z is significant then W is too. The relationship between Z and W is always going to be close according to their definitions. A reason for this corresponding pattern of significance, aside from the strong correlation between Z and W , is no doubt the fact that all significant cases here are the result of the presence of a single outlier.

The second step in this application of the method is to run all background samples of all sizes through the outlier screening procedure. The final result of this application is presented in Figure 9. The series of plots shown there reveal that 10 samples in total contain corrupt observations. There is no pattern concerning background sample types since all types (carbide, anthracite, SGB) seem prone to occasionally generating spurious data. The explanation for these unusual observations is not immediately apparent. These may be human recording errors, 'hic-ups' in the counter or genuine counts expressing moments in time in which irregular sample activities occur. (This last explanation is highly implausible in the extreme cases.) An exact explanation for these anomalous data may not be readily available but the treatment of them is straightforward. Such irregular observations are simply removed from the data. Therefore the absence of these observations from the analyses in section 2.2 turns out to be commendable in retrospect.

The removal of outliers from contaminated samples requires a method of identifying the offending observation(s). The method adopted is based on the results of the application of the Z and W statistics to the background data. If the Z and W statistics are both

Figure 9: plots of all background samples containing outliers.

counts per minute



significant or the Z statistic alone is significant, then the procedure is to simply to remove the observation x_i such that

$$\frac{|x_i - m|}{g^*} > \frac{|x_j - m|}{g^*}, \quad \forall j \neq i.$$

These standardised residuals give an indication of the relative excessiveness of each observation. Thus the most excessive observation is rejected. The fact that W may also be significant is outweighed by the fact that Z is significant. Priority is given to the latter statistic because of the strong empirical evidence which suggests that a single outlier is considerably more probable than an outlier-pair whenever both statistics are significant. However, if W should ever prove to be significant while Z turns out not to be significant, then an upper and lower outlier-pair is removed — that is, $x_{(1)}$ and $x_{(n)}$ are removed from the sample.

Once a sample has been decontaminated according to the above procedure, the trimmed sample is run through the detection process again to investigate for any secondary and lesser contamination. The process is continued until no further contamination is detected. Thus the outlier detection method is a recursive procedure. The problem of masking will make make the method inefficient if two outliers or more are close together and far apart from the other sample observations. Despite this drawback the method is still considered to be most effective for the single-outlier situation as the data application has shown and this may be all that is required for such small samples. The simplicity of the method makes it very easy to program. There is no claim that this is the most precise and efficient method available but from a merely pragmatic point of view it is recommended.

A final note is that only half of these outlying observations were detected at the original time of data processing. This study has therefore provided a safer and more efficient method of screening the data. It is also straightforward to implement and could be used in a wider capacity than the radiocarbon context. The method should not really be used, however, beyond the given range of sample sizes. This limits the method to small samples only. Extrapolation to larger sample sizes is not recommended since it is only an approximate method with all the inherent deficiencies attached to such approximation. It is essentially a pragmatic treatment of outliers developed on a simulation basis and was developed with the basic software limitations in mind.

3.4 Proof

• *proof for:*

The statistics G^* and " σ " (Downtown's estimator) are the same except for a multiplicative constant, where

$$G^* = \frac{2}{n(n-1)} \sum_{i=1}^{n-1} i(n-i)(X_{(i+1)} - X_{(i)})$$

and " σ " = $\frac{2\pi}{n(n-1)} \sum_{i=1}^n [i - \frac{1}{2}(n+1)] X_{(i)}$

Proof

$$\begin{aligned} & \sum_{i=1}^{n-1} i(n-i)(X_{(i+1)} - X_{(i)}) \\ &= \sum_{i=1}^{n-1} i(n-i)X_{(i+1)} - \sum_{i=1}^{n-1} i(n-i)X_{(i)} \\ &= \sum_{j=2}^n (j-1)(n-j+1)X_{(j)} - \sum_{j=1}^{n-1} j(n-j)X_{(j)} \\ &= (n-1)X_{(n)} + \sum_{j=2}^{n-1} [(j-1)(n-j+1) - j(n-j)]X_{(j)} - (n-1)X_{(1)} \\ &= (n-1)X_{(n)} + \sum_{j=2}^{n-1} [nj - j^2 + j - n + j - 1 - nj + j^2]X_{(j)} - (n-1)X_{(1)} \\ &= (n-1)X_{(n)} + \sum_{j=2}^{n-1} (2j - n - 1)X_{(j)} - (n-1)X_{(1)} \\ &= \sum_{j=1}^n (2j - n - 1)X_{(j)} \\ &= 2 \sum_{j=1}^n [j - \frac{1}{2}(n+1)]X_{(j)} \end{aligned}$$

The result now automatically follows.

4 Estimation of Background Activity

For this study, the data for any background sample in a single batch are assumed to belong to a simple white noise process around some constant underlying true mean value. The short counting series of 10 cycles and the results in section 2.2 make this a reasonable assumption. The physical interpretation of these true mean values is not straightforward. It is impossible to state with certainty that these values genuinely represent the true underlying background activity but this is largely a matter of trust in the materials, samples and the axioms of the radiocarbon dating principle in general. Sometimes the chemist may have cause to suspect that a material or a particular sample within a material is, in fact, unrepresentative of the true background activity. This may be due to experimental considerations but may also be due to statistical evidence provided by the analysis of data. This has occasionally happened in the course of laboratory practice when samples have been regarded as anomalous on the basis of their irregular activities and consequently rejected. Prior to this study, qualification of samples as 'irregular' has been a subjective consideration on the part of the chemist. A more objective approach would be preferred.

The first step, however, is to assess some simple properties of the data. The first property investigated is equality of background sample activities. It is of interest to see if sample activities are equal in each of the batches across time. A shift in true background activity over time would be expected, prior to analysis, to produce commensurate and uni-directional shifts in sample activities. Inequality of sample activities would bring the representative nature of the samples into question, i.e. "Are all background sample activities equally representative of the true background activity if they are significantly different from one another?" One solution to this question might be that it cannot definitely be known and that all sam-

ples should be given equal weight with no adjustments to the data. Another solution might be to dismiss certain samples on experimental/analytical grounds and retain a sub-set of samples for evaluation of the true activity. The latter solution up until the time of this study has been the one adopted by the laboratory.

Neither solution is optimal, the former being unrefined and the latter being wasteful. An alternative solution, and the one which is adopted here, is that each sample represents the true background activity plus some increase/decrease that relates to inherent properties of the particular sample or the vial in which it is counted. Ambers et al. [3] report that the glass vials used in liquid scintillation counting can introduce appreciable variation in the observed background activity and thus an irregular vial may result either in a decrease or an increase depending on its potassium content, this in itself dependent on the volume of glass. The fact that a decrease may occur means that the background sample with the lowest count rate is not necessarily the best representative of the true background activity.

In pursuit of an alternative solution it is first of all necessary to establish if background sample activities are consistently and significantly different from one another across time.

4.1 Sample Differences Across Time

The eight background samples investigated are paired off with each other according to their concurrence over the recorded batches. Table 5 shows the pattern of concurrence for paired samples.

The question of difference between samples breaks down into two parts:

- (a) Is the difference between samples constant over time?

Sample Pairs	Shared Batches	No. of Batches
(B35, B36)	1 - 6	6
(B37, B38a)	7 - 17 & 20 - 25	17
(B37, B38b)	7 - 17	11
(B37, B39)	7 - 17 & 20 - 25	17
(B37, B40)	7 - 17 & 20 - 25	17
(B38a, B38b)	7 - 17	11
(B38a, B39)	7 - 27	21
(B38a, B40)	7 - 27	21
(B38a, B41)	26 - 27	2
(B38b, B39)	7 - 17	11
(B38b, B40)	7 - 17	11
(B39, B40)	7 - 27	21
(B39, B41)	26 - 27	2
(B40, B41)	26 - 27	2

Table 5: pair-wise concurrence of samples across batches.

(b) If the difference *is* constant, is it significantly different from zero?

These two questions constitute a test for equality of sample activities.

4.1.1 Constancy of Sample Differences

To assess if the difference between samples is constant over time, each pair of samples that appear together across time are investigated. Since sample observations are paired according to batch cycles, the means of the batch cycle differences may be tested instead of the differences between batch means.

The test used to analyse these differences is just a straightforward analysis of variance. Expressing this test formally, let $X_{ik}^{(t)}$ be the variable denoting the cpm value of sample i in batch t at cycle k . The difference statistics for two samples i and j are thus defined

$$D_{(ij)k}^{(t)} = X_{ik}^{(t)} - X_{jk}^{(t)}, \quad \forall k, t$$

The statistics $\{D_{(ij)k}^{(t)}\}$ contain information about the difference between the samples. The superscript t is restricted to those batches in which the relevant samples appear together. The subscript k is relative to the batch and only includes instances of cycles at which activities are recorded for both samples. It is assumed that $\mathbf{E}(D_{(ij)k}^{(t)}) = \delta_{ij}^{(t)}$, $\forall k$, where $\delta_{ij}^{(t)}$ is the true underlying difference between samples i and j at batch t .

The estimator for mean batch cycle difference is simply

$$\bar{D}_{ij}^{(t)} = \frac{1}{n_{ij}^{(t)}} \sum_{k=1}^{n_{ij}^{(t)}} D_{(ij)k}^{(t)}$$

where $n_{ij}^{(t)}$ is the total number of difference statistics that can be evaluated for samples i and j at batch t . Due to the assumption about the expected value of the $\{D_{(ij)k}^{(t)}\}$, it can be seen that $\mathbf{E}(\bar{D}_{ij}^{(t)}) = \delta_{ij}^{(t)}$.

These means are used in the test of constancy of sample differences across time. The test of interest here can be suitably expressed as

$$\mathbf{H0} : \delta_{ij}^{(t_1)} = \delta_{ij}^{(t_2)} = \dots = \delta_{ij}^{(t_T)}$$

$$\text{v. } \mathbf{H1} : \{\delta_{ij}^{(t_u)}\} \text{ not all equal}$$

where the superscripts $\{t_u : u = 1, \dots, T\}$ denote the T batches in which the two samples concur. This is a simple test of the constancy of the difference between the two samples over time.

The results of the various analyses of variance are recorded in Table 6. From this table we can see that there are no significant results for any of the pairs of samples. In fact, the

Sample Differences	No. of Obsns.	No. of Batches	ANOVA RESULTS F-value	Significance
B35 - B36	60	6	1.68	< 0.01
B37 - B38a	157	17	0.52	< 0.01
B37 - B38b	101	11	0.53	< 0.01
B37 - B39	161	17	1.02	< 0.01
B37 - B40	60	6	1.54	< 0.01
B38a - B38b	102	11	1.02	< 0.01
B38a - B39	199	21	0.97	< 0.01
B38a - B40	96	10	0.82	< 0.01
B38a - B41	19	2	0.83	< 0.01
B38b - B39	102	11	1.09	< 0.01
B39 - B40	99	10	0.66	< 0.01
B39 - B41	19	2	0.08	< 0.01
B40 - B41	19	2	0.57	< 0.01

Table 6: one-way analysis of variance results for sample differences.

reported F-statistics are all low which indicates that there is little variation of the mean cycle differences across batches relative to the variation of the cycle differences within batches. The conclusion of this simple study, therefore, is that it is safe to assume that differences between samples remain constant over time even when shifts in the background activity occur. This is not to say, however, that these differences are significantly different from zero and this is the issue to which we now turn our attention.

4.1.2 Estimating Sample Differences

Having established that differences between samples are constant over time, it is now of interest to quantify these differences. Some questions are posed :-

- (1) Are samples significantly different from one another?
- (2) Are samples from the same material significantly different from one another?

(3) Are materials different from one another?

The results from this study will assist in answering these questions.

The estimation of sample differences is straightforward. From the preceding study concerning the constancy of sample differences, it can be asserted that $\mathbf{E}(D_{(ij)k}^{(t)}) = \delta_{ij}$, $\forall k, t$, where δ_{ij} is the difference between samples i and j . This difference is independent of time and, therefore, of shifts in background activity that may occur over time. An obvious unbiased estimate of δ_{ij} is therefore

$$\hat{\delta}_{ij} = [\sum_{u \in S_{ij}} n_{ij}^{(u)}]^{-1} \sum_{u \in S_{ij}} \sum_{k=1}^{n_{ij}^{(u)}} d_{(ij)k}^{(u)}$$

where S_{ij} denotes the set $\{t_1, t_2, t_3, \dots, t_T\}$ of all batches in which samples i and j appear together and the $\{d_{(ij)k}^{(u)}\}$ are the data realisations of the $\{D_{(ij)k}^{(u)}\}$. This is the simplest estimate to work with and the estimator from which it is derived is uniformly minimum variance unbiased. It is just the mean difference of the two samples over time.

Prediction intervals are constructed for the difference between all legitimate pairs of background samples. The form of these prediction intervals are

$$\hat{\delta}_{ij} \pm 2 \sqrt{\left(1 + \frac{1}{n_{ij}}\right)} \times \text{se}(\hat{\delta}_{ij})$$

where n_{ij} is the total number of observations used to evaluate $\hat{\delta}_{ij}$ and $\text{se}(\hat{\delta}_{ij})$ is the standard error of $\hat{\delta}_{ij}$. These intervals each specify an appropriate range of values in which an unseen measure of sample difference will fall with approximately 95% confidence. Sample differences are assumed to be independent and normally distributed. This assumption is founded on the

Differences	Estimates & Errors	Prediction Intervals
B35 - B36	-0.047 ± 0.087	$(-0.222, 0.128)$
B37 - B38a	0.274 ± 0.048	$(0.178, 0.370)^{\dagger}$
B37 - B38b	0.188 ± 0.057	$(0.073, 0.303)^{\dagger}$
B37 - B39	0.144 ± 0.047	$(0.050, 0.238)^{\dagger}$
B37 - B40	-0.130 ± 0.064	$(-0.259, -0.001)^{\dagger}$
B38a - B38b	-0.080 ± 0.059	$(-0.199, 0.039)$
B38a - B39	-0.127 ± 0.044	$(-0.215, -0.039)^{\dagger}$
B38a - B40	-0.418 ± 0.054	$(-0.527, -0.309)^{\dagger}$
B38a - B41	-3.379 ± 0.179	$(-3.746, -3.012)^{\dagger}$
B38b - B39	-0.053 ± 0.055	$(-0.164, 0.058)$
B39 - B40	-0.287 ± 0.058	$(-0.404, -0.170)^{\dagger}$
B39 - B41	-3.274 ± 0.150	$(-3.582, -2.966)^{\dagger}$
B40 - B41	-3.061 ± 0.184	$(-3.439, -2.683)^{\dagger}$

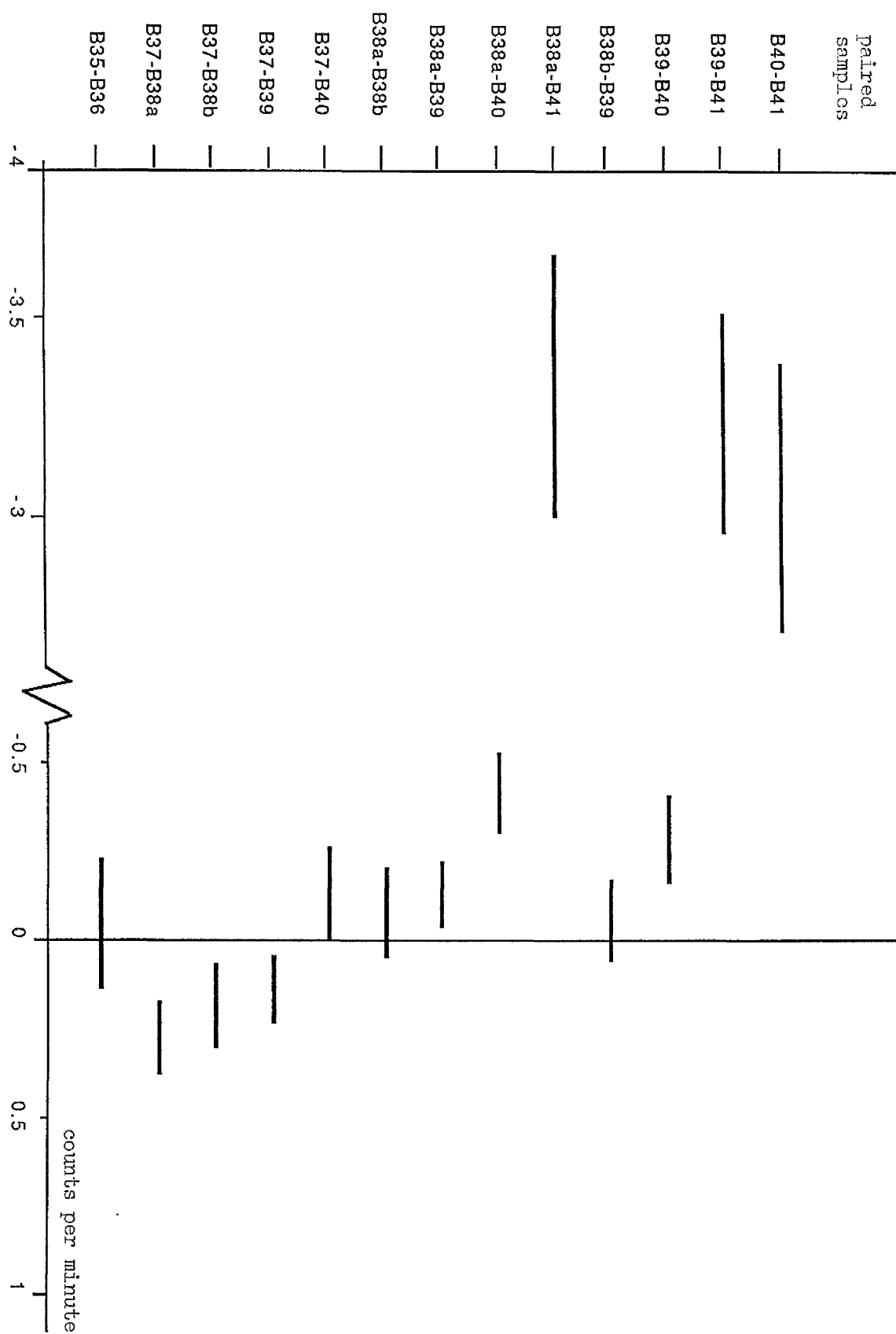
Table 7: prediction intervals for sample differences. Intervals marked \dagger do not contain the value zero.

evidence of individual sample observations being independent and normally distributed (see section 2.2). From that evidence and the fact that the difference of two Gaussian statistics is itself Gaussian, it can be taken that this assumption is reasonable.

Table 7 shows the results of this study and Figure 10 presents the prediction intervals in graphical form. The prediction intervals indicate a fair amount :-

- (1) Samples are generally different from one another. Only 3 of the 13 pairs of samples produce prediction intervals containing the value zero.
- (2) Samples within materials are found to be different in some cases. Calcium carbide appears to be relatively stable in that differences between carbide samples all turn out to be not significantly different from zero. Anthracite, on the other hand, appears to be relatively unstable in that differences between pairs of anthracite samples all significantly deviate from zero. This may suggest an unsuitability of material. Indeed, at the time of this study certain chemists working with anthracite were not

Figure 10: prediction intervals for differences between background samples.



entirely satisfied with its performance. As a result, the tendency has often been to drop the recorded data for anthracite samples from the overall calculation of background activity.

- (3) Materials themselves are manifestly different from one another. Anthracite proves to be consistently different from both calcium carbide and SGB. The data suggest that the activities of anthracite samples are consistently higher than the activities of the samples belonging to other materials. This may suggest that anthracite is more inherently corrupt or corruptible than other materials. It is not possible to offer a precise reason here since this is not primarily a statistical matter. The results of this analysis, however, may suggest that this is a matter worthy of further investigation. One of the prediction intervals also shows that the SGB sample is significantly different from one of the carbide samples although it is not significantly different from another carbide sample. This result also leaves scope for further investigation.

- (4) One anthracite sample, namely B41, appears to be a corrupt sample since it is radically different from all other samples including another anthracite sample B40. The data from this sample are clearly anomalous.

It is clear that samples and materials both contribute considerably to significant differences among the data. Recognising that samples are significantly different from one another presents us with the problem of suitably managing the data with a view to estimating the background activity.

4.2 In Search of the Background Activity

The standard laboratory practice of calculating background activity has been to pool data from selected background samples over a number of consecutive batches. Selection of samples has been at the discretion of the chemist. This method has certain weaknesses :-

- (1) Significant variation of the background activity may occur across time. Pooling of information across batches is not therefore recommended unless performed with due consideration of potential significant variation across time. More local estimates of background activity such as individual batch estimates — if these can be produced with reasonably small errors — may be more appropriate.
- (2) Significant differences can exist between the different background materials as previously demonstrated. Significant differences can also exist between the individual background samples, even between samples stemming from the same source material. As such, it is not clear what a pooled estimate of the samples is truly representing. It may be better to consider a different estimation approach which allows for the possibility that not all samples are equally representative of the true background activity. This approach does not have to incur the rejection of samples.
- (3) Rejection of samples for the purpose of estimation is not optimal. All samples provide information concerning the background activity. Information from less representative samples can be extracted by applying suitable corrections to the data from these samples. Retaining all samples is a more economical treatment of the data and will also produce more precise estimates of the background activity. Of course, from an experimental point of view it is preferable to drop less reliable materials/samples

once they are identified as such and substitute them with better replacements. However, given that the data for a batch stand unalterable once recorded, it is required to develop a treatment of the data which does not dispense with any of the data.

A different approach to estimation of the background activity is therefore clearly desirable if such an approach can be found. The one that is adopted here considers that some samples are better indicators of the true background activity than others but that the poorer indicators are also valuable sources of information. The good indicators of the true background activity will be known as *aligned samples* and those that are not so good will be known as *unaligned samples*. The latter samples are those whose activities are significantly shifted away from the true background activity due to certain factors. These factors may be qualifiable according to the chemist's knowledge of the samples and the experimental procedures applied to them.

The data from aligned and unaligned samples are combined in a suitable way, providing an estimate for the background activity. These estimates are local to each batch and are not based on combining estimates from different batches. The concern that this might produce estimates with unacceptably large errors will be shown to be unfounded. For the sake of simplicity, the method is developed for the case in which we are dealing with a single aligned sample and a group of unaligned samples. This is essentially unrealistic but the method can easily be extended to the case in which several aligned samples are employed with only one or two samples considered to be unaligned (see section 4.2.6).

In estimating the background activity for some particular batch, the method here uses information from batches preceding and succeeding the relevant batch as well as from the batch itself. (Normally a series of batches is recorded before sample ages are finally submit-

ted.) This pool of batches is used to calculate the shifts from the true background activity incurred by each unaligned sample, these shifts being estimated from the differences between each unaligned sample and the aligned sample across time. It has already been established that the difference between two samples is independent of and constant over time (see section 4.1.1). (Note: pooling of batches is performed here in a different context to the pooling of batch estimates of the background activity and, as such, avoids the criticism that has been made concerning the latter kind of pooling.)

Data pertaining to unaligned samples with respect to the relevant batch are subsequently corrected according to the estimated shifts. Once the data are thus corrected, a simple batch average of the corrected sample activities is evaluated. The shifts used to correct the data inevitably contribute to the overall error of the estimated background activity but over an increasing number of batches this error contribution is negligible compared to the sample activity errors themselves.

Due to the fact that the method uses information from a batch and its neighbouring batches in either direction, the estimator that is derived from this method will be known as the *circumspect estimator*.

4.2.1 Choosing an Aligned Sample

The choice of an aligned sample is obviously an influential factor in the analysis. The determination of a sample as being aligned is taken here to be directly related to the reliability of the sample. The reliability of a sample may be ascertained from experimental/analytical considerations. Simple plots of the data may help the chemist to make a decision. A chemist

working over a long period with materials and samples is also likely to develop an instinct with regard to the reliability of materials and samples. The choice of aligned sample should therefore draw on experimental and statistical knowledge. It may even be that all samples would be considered reliable (years of experimental practice would almost certainly reduce trial and error in producing samples) in which case all samples would be considered aligned and no corrections to the data would be required. A simple batch average would then be calculated for background activity. For the sake of development of the method, however, one sample is chosen to be aligned and the extension to several aligned samples is considered later.

In the realistic approach it would be more likely that a sample would be identified as unaligned and treated accordingly rather than it being identified as aligned. This is because it is more natural to identify irregularity than it is to identify regularity. (It is easier to spot someone who stands out from a crowd than it is to spot a conformist.) If a sample proves to be relatively inconsistent or uncharacteristic, then it may then be classified as unaligned and suitably corrected. This would be the reasonable approach in practice. Despite the artificial nature of choosing an aligned sample, however, the method proceeds as it stands since it may be adapted at a later stage to accommodate a more realistic approach.

It must be stressed here that the choice of an aligned sample in this particular study is largely an arbitrary one for the sake of developing the method and is not based on a background sample possessing the lowest count rate. Such a sample would provide no guarantee whatsoever of being the most reliable sample in terms of representing the true background activity (this has already been stated). It is thus good to keep in mind the essentially unrealistic nature of choosing an aligned sample with a view to taking a more

realistic approach after the method is developed.

4.2.2 Notation

Before proceeding to the formal details of the method, it is necessary to present some notation. This notation provides a menu of the terms that will appear in the rest of this section.

1. S_B = set of all relevant batches
2. $X_{ik}^{(t)}$ = variable representing cpm value for the i th background
sample at k th cycle in batch t
3. $n_i^{(t)}$ = number of cpm values for i th sample in batch t
 $n_{ij}^{(t)}$ = number of pairwise cpm values for background
samples i and j in batch t
 $n_{ijm}^{(t)}$ = number of triple-wise cpm values for background
samples i, j and m in batch t
4. S_{ij} = set of all batches containing background samples i and j ($S_{ij} \subseteq S_B$)
 S_{ijm} = set of all batches containing background samples i, j and m
i.e. $S_{ijm} = S_{ij} \cap S_{im}$
5. $h^{(t)}$ = total number of background samples in batch t
 $n^{(t)}$ = total number of cpm values pertaining to all background
samples in batch t , i.e. $n^{(t)} = \sum_{i=1}^{h^{(t)}} n_i^{(t)}$

The method proceeds with the assumption that $h^{(t)} \geq 3$. This is virtually always the case and the standard practice is to record 4 background samples in any one batch. The

case $h^{(t)} = 2$ is not presented here although it would be a fairly simple matter to adapt the method to this case.

4.2.3 Description of the Data

Suppose that a number of batches have been recorded over which a sizable amount of data has been obtained. For some particular batch t the random variables pertaining to the relevant background samples are

$$X_{ik}^{(t)}, \quad i = 1, \dots, h^{(t)}, \quad k = 1, \dots, n_i^{(t)}$$

Taking sample a to be the aligned sample and applying the expectation operator, it is assumed that

$$\left. \begin{aligned} \mathbf{E}(X_{ak}^{(t)}) &= \mu^{(t)}, & k &= 1, \dots, n_a^{(t)} \\ \mathbf{E}(X_{ik}^{(t)}) &= \mu^{(t)} + \delta_i, & i &\neq a, \quad k = 1, \dots, n_i^{(t)} \end{aligned} \right\} \quad (\text{A4.1})$$

where $\mu^{(t)}$ is the true underlying background activity at batch t and δ_i is the true shift from the background activity incurred by unaligned sample i . Some further assumptions are made here concerning the independence of the variables :-

$$(\text{A4.2}) \quad \mathbf{Cov}(X_{ik}^{(t)}, X_{il}^{(t)}) = 0, \quad \forall i, k, l, t, k \neq l$$

$$(\text{A4.3}) \quad \mathbf{Cov}(X_{ik}^{(t)}, X_{jl}^{(t)}) = 0, \quad \forall i, j, k, l, t, i \neq j$$

$$(\text{A4.4}) \quad \mathbf{Cov}(X_{ik}^{(t)}, X_{jl}^{(u)}) = 0, \quad \forall i, j, k, l, t, u, t \neq u$$

Assumptions (A4.2) – (A4.4) are supported by the correlation study results in section 2.2.1.

4.2.4 Correcting Unaligned Samples

The method for correcting unaligned samples is straightforward. Suppose an estimate of background activity is required for some batch t . The aligned sample is taken to be a good representative of the true background activity and so does not require correction. The other samples must be corrected, however, and this requires us to estimate the shift from the true background activity incurred by these samples. A simple estimator for the shift pertaining to an unaligned sample i is

$$D_i = n_{ai}^{-1} \sum_{u \in S_{ai}} \sum_{k=1}^{n_{ai}^{(u)}} (X_{ak}^{(u)} - X_{ik}^{(u)}), \quad n_{ai} = \sum_{u \in S_{ai}} n_{ai}^{(u)}$$

The above statistic is just the mean difference between sample a and sample i over time. This is determined over all batches in which sample a appears with sample i (preceding/succeeding/including batch t). The estimator D_i is the estimator of sample shift. It is an appealing estimator because it is simple and due to assumption (A4.1) it is an unbiased estimator of the true shift δ_i . The corrections suggested by this estimator give rise to the variables

$$Y_{ik}^{(t)} = X_{ik}^{(t)} - D_i, \quad i = 1, \dots, h^{(t)}, k = 1, \dots, n_i^{(t)}, D_a = 0$$

The above corrections are suitable since they yield the desirable property that $E(Y_{ik}^{(t)}) = \mu^{(t)}, \forall i, k$. They are the simplest corrections yielding this property of unbiasedness.

4.2.5 An Estimator of Background Activity

The natural estimator of background activity once the corrections have been taken into account is

$$\bar{Y}^{(t)} = \frac{1}{n^{(t)}} \sum_{i=1}^{h^{(t)}} \sum_{k=1}^{n_i^{(t)}} Y_{ik}^{(t)}$$

This is an unbiased estimator of $\mu^{(t)}$. It is also possible to construct some weighted average of the $\{Y_{ik}^{(t)}\}$ although this is not pursued here.

To derive the error of $\bar{Y}^{(t)}$, it is assumed that each uncorrected sample i has an error $\sigma_i^{(t)}$ associated with it: this applies to both aligned and unaligned samples. The error of each shift estimator D_i is taken to be τ_i . The derivation of the actual error of $\bar{Y}^{(t)}$ is based on certain results :-

$$(E4.1) \quad \text{Var}(Y_{ak}^{(t)}) = [\sigma_a^{(t)}]^2$$

$$(E4.2) \quad \text{Var}(Y_{ik}^{(t)}) = n_{ai}^{-1} (n_{ai} - 2) [\sigma_i^{(t)}]^2 + \tau_i^2, \quad i \neq a$$

$$(E4.3) \quad \text{Cov}(Y_{ak}^{(t)}, Y_{il}^{(w)}) = n_{ai}^{-1} [\sigma_a^{(t)}]^2, \quad i \neq a$$

$$(E4.4) \quad \text{Cov}(Y_{ik}^{(t)}, Y_{il}^{(w)}) = -2 n_{ai}^{-1} [\sigma_i^{(t)}]^2 + \tau_i^2, \quad i \neq a, (k, t) \neq (l, w)$$

$$(E4.5) \quad \text{Cov}(Y_{ik}^{(t)}, Y_{jl}^{(w)}) = n_{ai}^{-1} n_{aj}^{-1} \sum_{u \in S_{aij}} n_{aij}^{(u)} [\sigma_a^{(u)}]^2, \quad i \neq j \neq a$$

The proofs of (E4.1)–(E4.5) are given in (P4.1) at the end of this section.

With these results and a bit of algebraic manipulation it can be shown that

$$\begin{aligned}
[n^{(t)}]^2 \text{Var}(\bar{Y}^{(t)}) &= n_a^{(t)} (1 + 2 \underbrace{\sum_{\substack{i=1 \\ i \neq a}}^{h^{(t)}}} n_{ai}^{-1} n_i^{(t)}) [\sigma_a^{(t)}]^2 \\
&\dots + \underbrace{\sum_{\substack{i=1 \\ i \neq a}}^{h^{(t)}}} n_{ai}^{-1} n_i^{(t)} (n_{ai} - 2n_i^{(t)}) [\sigma_i^{(t)}]^2 \\
&\dots + \underbrace{\sum_{\substack{i=1 \\ i \neq a}}^{h^{(t)}}} [n_i^{(t)}]^2 \tau_i^2 \\
&\dots + \underbrace{\sum_{\substack{i=1 \\ i \neq j \neq a}}^{h^{(t)}-1} \sum_{j=i+1}^{h^{(t)}}} 2 n_{ai}^{-1} n_{aj}^{-1} n_i^{(t)} n_j^{(t)} \sum_{u \in S_{aij}} n_{aij}^{(u)} [\sigma_a^{(u)}]^2}
\end{aligned}$$

The proof of this result is given in (P4.2) at the end of the section. The four components of the right-hand term above are the contributions to the total variance from the aligned sample, the unaligned samples and the shifts (both variances and covariances).

Replacing the variables $\{Y_{ik}^{(t)}\}$ by the data realisations $\{y_{ik}^{(t)}\}$ it is possible to construct an approximate 95% confidence interval for the true background activity in batch t , namely

$$\hat{\mu}^{(t)} \pm 2 \text{se}(\hat{\mu}^{(t)}) \quad (\text{E4.6})$$

with

$$\begin{aligned}
\hat{\mu}^{(t)} &= \bar{y}^{(t)} = \frac{1}{n^{(t)}} \sum_{i=1}^{h^{(t)}} \sum_{k=1}^{n_i^{(t)}} y_{ik}^{(t)} \\
\text{se}(\hat{\mu}^{(t)}) &= [n^{(t)}]^{-1} \times \left\{ n_a^{(t)} \left(1 + 2 \sum_{\substack{i=1 \\ i \neq a}}^{h^{(t)}} n_{ai}^{-1} n_i^{(t)} \right) [\hat{\sigma}_a^{(t)}]^2 \right. \\
&\quad \dots + \sum_{\substack{i=1 \\ i \neq a}}^{h^{(t)}} n_{ai}^{-1} n_i^{(t)} (n_{ai} - 2n_i^{(t)}) [\hat{\sigma}_i^{(t)}]^2 \\
&\quad \dots + \sum_{\substack{i=1 \\ i \neq a}}^{h^{(t)}} [n_i^{(t)}]^2 \hat{\tau}_i^2 \\
&\quad \left. \dots + \sum_{\substack{i=1 \\ i \neq j \neq a}}^{h^{(t)}-1} \sum_{j=i+1}^{h^{(t)}} 2 n_{ai}^{-1} n_{aj}^{-1} n_i^{(t)} n_j^{(t)} \sum_{u \in S_{aij}} n_{aij}^{(u)} [\hat{\sigma}_a^{(u)}]^2 \right\}^{\frac{1}{2}}
\end{aligned}$$

The terms $\{\hat{\sigma}_i^{(i)}\}$ and $\{\hat{\tau}_i\}$ are, respectively, the standard errors for the estimates of sample activities and the estimates of sample shifts.

4.2.6 Extending to a Group of Aligned Samples

Extending the method makes it possible to work with a group of aligned samples rather than a single aligned sample. In practice, this would be much more realistic.

To extend the method, it is necessary to redefine the estimator of shift incurred by an unaligned sample. The definition, as it stands, constitutes the difference over time between a single aligned sample and the relevant unaligned sample. This cannot apply when there are several aligned samples.

In dealing with a group of aligned samples — these being distinguished in the realistic

scenario by the identification of perhaps one or two unaligned samples — an average should be calculated at each cycle for all aligned samples with respect to all relevant batches. Then the differences between these cycle averages and the corresponding cycles for some particular unaligned sample may be evaluated. The mean of these differences is then an unbiased estimate for the shift incurred by the particular unaligned sample.

With this suitable modification, the resultant estimate of background activity is still the batch mean of the corrected data. The error of the estimate will be more complex, however, but with some algebraic manipulation it should be possible to derive an exact estimate of the error. The estimate and error for the extended case is not presented here.

4.2.7 Data Application of Method

Table 8 presents estimates of the background activity for the data which appears in this study using the circumspect estimate of the background activity. These estimates are derived with carbide sample B38a selected as the aligned sample. (This sample is the only carbide sample appearing in all batches after batch 6 and stems from a source material that was observed to be relatively reliable according to the conclusions presented in section 4.1.2. This makes it a suitable candidate for an aligned sample although it is not claimed here that it is the most reliable sample that could have been chosen.)

The circumspect estimates are presented along with laboratory estimates provided by Dr. Mike Stenhouse for this particular set of data. The former estimates are derived using all samples in each individual batch while the latter estimates are derived by pooling selected samples and batches.

Batch	No. of Obsns.	Estimates & Errors <i>Circumspect</i>	Estimates & Errors <i>Laboratory</i>
7	39	6.453 ± 0.083	6.39 ± 0.031
8	38	6.233 ± 0.062	
9	35	6.581 ± 0.067	6.72 ± 0.097
10	40	6.663 ± 0.078	
11	40	6.768 ± 0.072	
12	40	6.577 ± 0.075	
13	19	6.611 ± 0.086	
14	40	6.593 ± 0.063	
15	39	6.610 ± 0.079	
16	40	6.737 ± 0.073	
17	44	6.719 ± 0.075	
18	29	6.521 ± 0.095	6.53 ± 0.135
19	30	6.548 ± 0.056	
20	39	6.382 ± 0.068	
21	40	6.215 ± 0.072	6.26 ± 0.075
22	39	6.095 ± 0.074	
23	39	6.253 ± 0.062	
24	40	6.140 ± 0.058	
25	40	6.158 ± 0.071	
26	39	6.336 ± 0.091	
27	40	6.243 ± 0.081	

Table 8: circumspect and laboratory estimates.

Batch	Estimates & Errors <i>Retrospect</i>	Estimates & Errors <i>Circumspect</i>
7	6.386 \pm 0.100	6.453 \pm 0.083
8	6.199 \pm 0.101	6.233 \pm 0.062
9	6.642 \pm 0.084	6.581 \pm 0.067
10	6.706 \pm 0.088	6.663 \pm 0.078
11	6.751 \pm 0.082	6.768 \pm 0.072
12	6.549 \pm 0.083	6.577 \pm 0.075
13	6.584 \pm 0.097	6.611 \pm 0.086
14	6.573 \pm 0.071	6.593 \pm 0.063
15	6.598 \pm 0.085	6.610 \pm 0.079
16	6.694 \pm 0.078	6.737 \pm 0.073
17	6.682 \pm 0.078	6.719 \pm 0.075
18	6.517 \pm 0.116	6.521 \pm 0.095
19	6.530 \pm 0.064	6.548 \pm 0.056
20	6.358 \pm 0.085	6.382 \pm 0.068
21	6.168 \pm 0.075	6.215 \pm 0.072
22	6.072 \pm 0.077	6.095 \pm 0.074
23	6.237 \pm 0.063	6.253 \pm 0.062
24	6.127 \pm 0.060	6.140 \pm 0.058
25	6.152 \pm 0.072	6.158 \pm 0.071

Table 9: retrospect and circumspect estimates.

An examination of Table 8 shows that the errors associated with the circumspect estimates are comparable, if not favourable, to the errors associated with the laboratory estimates. It is not clear how the error recorded for the laboratory estimate relating to batches 7 and 8 can be so small but, this aside, the comparison of the two sets of estimates demonstrates that the circumspect estimate is a relatively compact estimate. It also appears to produce errors that are generally superior to those of the given laboratory estimates.

4.2.8 Variation on a Theme

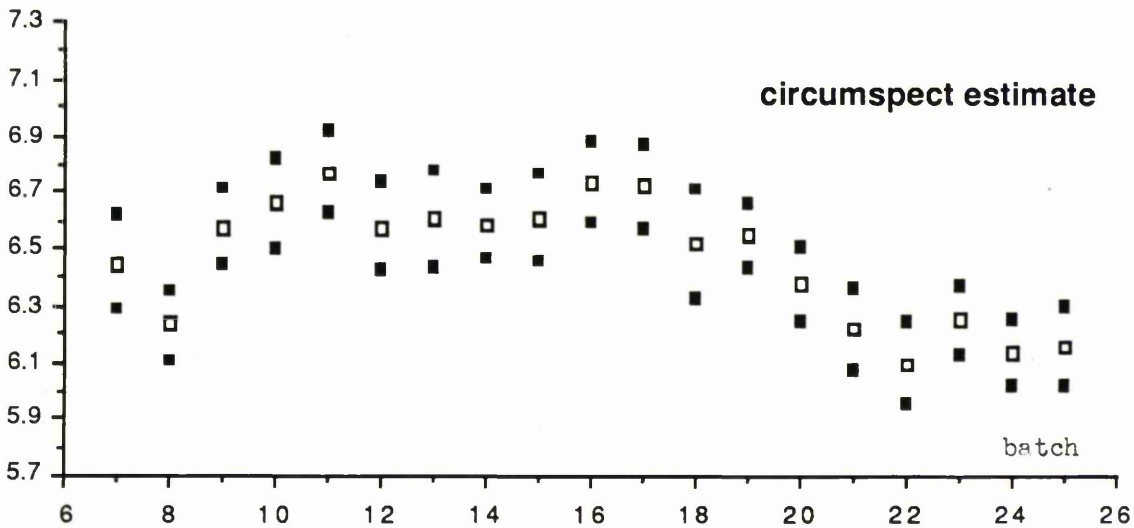
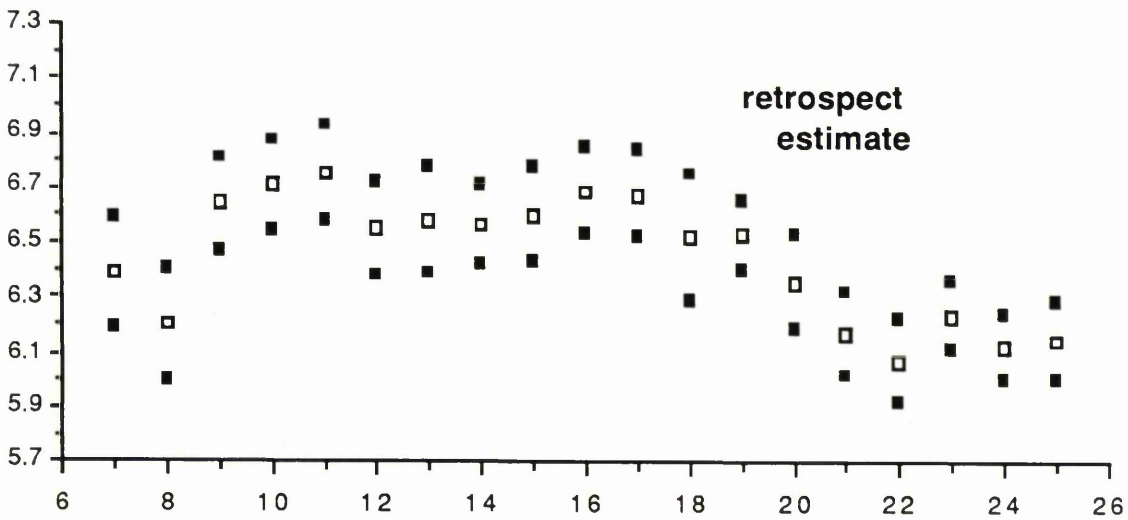
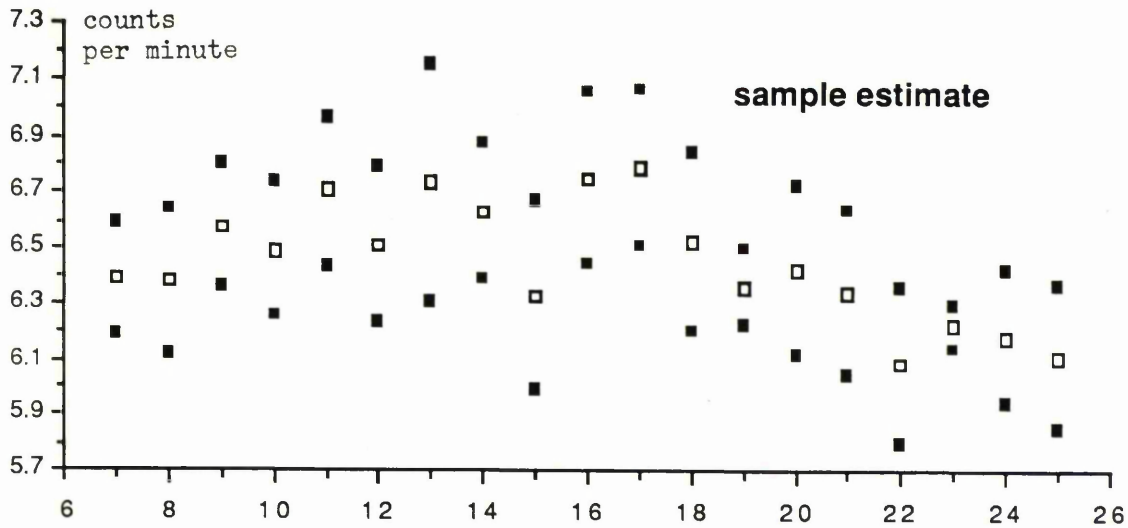
One problem with the circumspect estimator of background activity is that it generally requires data to be amassed over an interval of time extending beyond each batch that is

to be processed. Standard laboratory practice is normally to do this anyway, so this is not entirely unacceptable. If this is considered undesirable, however, the objection may be overcome by a simple restriction on the circumspect estimator. By stipulating that a batch may only use information from preceding batches, it is possible to construct a specialised case of the circumspect estimator which for obvious reasons will be called the *retrospect estimator*. Retrospect estimates may be evaluated immediately without having to wait for more data to be amassed, presuming that a history of data or some useful summary statistics from that data are accessible.

Table 9 shows the retrospect and circumspect estimates for batches 7–25. It can be seen that the initial errors for the retrospect estimates are relatively large since the retrospect estimates do not have the advantage of ‘looking forward’. As time progresses, however, this advantage diminishes until it is negligible. This happens fairly quickly — about 4 or 5 batches.

Plots for these estimates appear in Figure 11 along with a plot of the aligned sample B38a. The plots show interval estimates (95% confidence) for each type of background activity estimator (single sample/retrospect/circumspect). The plots provide two main points of interest. The first point is that the estimates pertaining to the aligned sample are not entirely indicative of the retrospect and circumspect estimates which draw on this sample as a baseline. This shows that the retrospect and circumspect estimates, although necessarily influenced by the aligned sample, are not entirely dominated by it. This is obviously desirable. The errors of the aligned sample estimates are also relatively large (as would be expected) and they do not reveal the subtle pattern of the background activity over time that the other two sets of estimates clearly reveal.

Figure 11: interval estimates for three estimates of the background activity



The second point to note from these plots is that there is no great advantage, estimate and error-wise, of the circumspect estimates over the retrospect estimates. This means that it is probably just as well to use the latter estimates since they may be evaluated immediately at the time of recording.

The pattern of background activity across time also suggests that the pooling of data over indiscriminate time intervals is unwise. The pooling which has been done with respect to the laboratory estimates (see Table 8, page 81), however, appears to have been performed over intervals of relative constancy in the background activity — certainly with respect to the picture of the background activity provided by the retrospect estimates in Figure 11. Pooling will be sensible if due regard is given to the trend of background activity over time and this appears to have been the case here. On the whole, however, retrospect estimation may offer a more useful way of estimating background activity since it does not pool data across batches incorporating possible time trends and also produces reasonably compact errors.

4.3 Proofs of Results

Proof (P4.1) of results (E4.1)–(E4.5)

- *proof for (E4.1) :* $\text{Var}(Y_{ak}^{(t)}) = [\sigma_a^{(t)}]^2$.

$$\begin{aligned}
 \text{Var}(Y_{ak}^{(t)}) &= \text{Var}(X_{ak}^{(t)} - D_a) && \text{by definition} \\
 &= \text{Var}(X_{ak}^{(t)}) && \text{since } D_a = 0 \\
 &= [\sigma_a^{(t)}]^2
 \end{aligned}$$

- *proof for (E4.2) :* $\text{Var}(Y_{ik}^{(t)}) = n_{ai}^{-1}(n_{ai} - 2)[\sigma_i^{(t)}]^2 + \tau_i^2, \quad i \neq a$.

$$\begin{aligned}
 \underbrace{\text{Var}(Y_{ik}^{(t)})}_{i \neq a} &= \text{Var}(X_{ik}^{(t)} - D_i) && \text{by definition} \\
 &= \text{Var}(X_{ik}^{(t)}) + \text{Var}(D_i) - 2 \text{Cov}(X_{ik}^{(t)}, D_i) \\
 &= [\sigma_i^{(t)}]^2 + \tau_i^2 - 2 \text{Cov}(X_{ik}^{(t)}, n_{ai}^{-1} \sum_{u \in S_{ai}} \sum_{l=1}^{n_{ai}^{(u)}} (X_{il}^{(u)} - X_{al}^{(u)})) \\
 &= [\sigma_i^{(t)}]^2 + \tau_i^2 - 2 n_{ai}^{-1} \sum_{u \in S_{ai}} \sum_{l=1}^{n_{ai}^{(u)}} [\text{Cov}(X_{ik}^{(t)}, X_{il}^{(u)}) \\
 &\quad \dots - \text{Cov}(X_{ik}^{(t)}, X_{al}^{(u)})] \\
 &= [\sigma_i^{(t)}]^2 + \tau_i^2 - 2 n_{ai}^{-1} [\sigma_i^{(t)}]^2 && \text{by A(4.2)–A(4.4)} \\
 &= n_{ai}^{-1}(n_{ai} - 2)[\sigma_i^{(t)}]^2 + \tau_i^2
 \end{aligned}$$

- *proof for (E4.3) :* $\text{Cov}(Y_{ak}^{(t)}, Y_{il}^{(w)}) = n_{ai}^{-1} [\sigma_a^{(t)}]^2, \quad i \neq a.$

$$\begin{aligned}
\underbrace{\text{Cov}(Y_{ak}^{(t)}, Y_{il}^{(w)})}_{i \neq a} &= \text{Cov}(X_{ak}^{(t)}, X_{il}^{(w)} - D_i) \\
&= -\text{Cov}(X_{ak}^{(t)}, D_i) && \text{by (A4.2)–(A4.4)} \\
&= -n_{ai}^{-1} \sum_{u \in S_{ai}} \sum_{l=1}^{n_{ai}^{(u)}} \text{Cov}(X_{ak}^{(t)}, X_{il}^{(u)} - X_{al}^{(u)}) \\
&= n_{ai}^{-1} [\sigma_a^{(t)}]^2
\end{aligned}$$

- *proof for (E4.4) :* $\text{Cov}(Y_{ik}^{(t)}, Y_{il}^{(w)}) = -2 n_{ai}^{-1} [\sigma_i^{(t)}]^2 + \tau_i^2, \quad i \neq a, (k, t) \neq (l, w).$

$$\begin{aligned}
\text{Cov}(Y_{ik}^{(t)}, Y_{il}^{(w)}) &= \text{Cov}(X_{ik}^{(t)} - D_i, X_{il}^{(w)} - D_i) \\
&= -2 \text{Cov}(X_{ik}^{(t)}, D_i) + \text{Var}(D_i) && \text{by (A4.2)–(A4.4)} \\
&= -2 n_{ai}^{-1} [\sigma_i^{(t)}]^2 + \tau_i^2 && \text{see proof for (E4.2)}
\end{aligned}$$

- *proof for (E4.5) :* $\text{Cov}(Y_{ik}^{(t)}, Y_{jl}^{(w)}) = n_{ai}^{-1} n_{aj}^{-1} \sum_{u \in S_{aij}} n_{aij}^{(u)} [\sigma_a^{(u)}]^2, \quad i \neq j \neq a.$

$$\begin{aligned}
\underbrace{\text{Cov}(Y_{ik}^{(t)}, Y_{jl}^{(w)})}_{i \neq j \neq a} &= \text{Cov}(X_{ik}^{(t)} - D_i, X_{jl}^{(w)} - D_j) \\
&= \text{Cov}(D_i, D_j) && \text{by (A4.2)–(A4.4)} \\
&= \text{Cov}\left(n_{ai}^{-1} \sum_{r \in S_{ai}} \sum_{p=1}^{n_{ai}^{(r)}} (X_{ip}^{(r)} - X_{ap}^{(r)}), \right. \\
&\quad \left. \dots n_{aj}^{-1} \sum_{s \in S_{aj}} \sum_{q=1}^{n_{aj}^{(s)}} (X_{jq}^{(s)} - X_{aq}^{(s)})\right) \\
&= n_{ai}^{-1} n_{aj}^{-1} \sum_{r \in S_{ai}} \sum_{s \in S_{aj}} \sum_{p=1}^{n_{ai}^{(r)}} \sum_{q=1}^{n_{aj}^{(s)}} \text{Cov}(X_{ap}^{(r)}, X_{aq}^{(s)}) \\
&= n_{ai}^{-1} n_{aj}^{-1} \sum_{u \in S_{aij}} n_{aij}^{(u)} [\sigma_a^{(u)}]^2
\end{aligned}$$

This last result is not entirely intuitive and needs to be explained. It must be noted that S_{ai} is not necessarily the same as S_{aj} and nor is $n_{ai}^{(t)}$ necessarily the same as $n_{aj}^{(t)}$ even if

$t \in S_{ai}$ and $t \in S_{aj}$. From the various assumptions that have been asserted we have

$$\left. \begin{aligned} \text{Cov}(X_{ap}^{(r)}, X_{aq}^{(s)}) &= [\sigma_a^{(r)}]^2, \quad s = r, p = q \\ &= 0, \quad \text{elsewhere} \end{aligned} \right\}$$

Thus the only relevant batches are those in the intersection of S_{ai} and S_{aj} , i.e. S_{aij} . For any batch $u \in S_{aij}$, there will be $n_{aij}^{(u)}$ complete triple-wise observations. Hence result.

Proof (P4.2) of error for $\bar{Y}^{(t)}$

- *proof for :*

$$\begin{aligned}
 [n_{(t)}]^2 \text{Var}(\bar{Y}^{(t)}) &= n_a^{(t)} \left(1 + 2 \underbrace{\sum_{\substack{i=1 \\ i \neq a}}^{h^{(t)}}} n_{ai}^{-1} n_i^{(t)}\right) [\sigma_a^{(t)}]^2 \\
 &\dots + \underbrace{\sum_{\substack{i=1 \\ i \neq a}}^{h^{(t)}}} n_{ai}^{-1} n_i^{(t)} (n_{ai} - 2 n_i^{(t)}) [\sigma_a^{(t)}]^2 \\
 &\dots + \underbrace{\sum_{\substack{i=1 \\ i \neq a}}^{h^{(t)}}} [n_i^{(t)}]^2 \tau_i^2 \\
 &\dots + \underbrace{\sum_{i=1}^{h^{(t)}-1} \sum_{j=i+1}^{h^{(t)}}}_{i \neq j \neq a} 2 n_{ai}^{-1} n_{aj}^{-1} n_i^{(t)} n_j^{(t)} \sum_{u \in S_{aij}} n_{aij}^{(u)} [\sigma_a^{(u)}]^2
 \end{aligned}$$

The following proof makes use of results (E4.1)–(E4.5) :-

$$\begin{aligned}
 [n^{(t)}]^2 \text{Var}(\bar{Y}^{(t)}) &= \text{Var}(\sum_{i=1}^{h^{(t)}} \sum_{k=1}^{n_i^{(t)}} Y_{ik}^{(t)}) \\
 &= \text{Cov}(\sum_{i=1}^{h^{(t)}} \sum_{k=1}^{n_i^{(t)}} Y_{ik}^{(t)}, \sum_{j=1}^{h^{(t)}} \sum_{l=1}^{n_j^{(t)}} Y_{jl}^{(t)}) \\
 &= \sum_{i=1}^{h^{(t)}} \sum_{k=1}^{n_i^{(t)}} \sum_{j=1}^{h^{(t)}} \sum_{l=1}^{n_j^{(t)}} \text{Cov}(Y_{ik}^{(t)}, Y_{jl}^{(t)})
 \end{aligned}$$

$$\begin{aligned}
&= \sum_{k=1}^{n_a^{(t)}} \mathbf{Var}(Y_{ak}^{(t)}) + \underbrace{\sum_{i=1}^{h^{(t)}}}_{i \neq a} \sum_{k=1}^{n_i^{(t)}} \mathbf{Var}(Y_{ik}^{(t)}) \\
&\dots + \underbrace{\sum_{k=1}^{n_a^{(t)}} \sum_{l=1}^{n_a^{(t)}}}_{k \neq l} \mathbf{Cov}(Y_{ak}^{(t)}, Y_{al}^{(t)}) \\
&\dots + \underbrace{\sum_{i=1}^{h^{(t)}}}_{i \neq a} \underbrace{\sum_{k=1}^{n_i^{(t)}} \sum_{l=1}^{n_i^{(t)}}}_{k \neq l} \mathbf{Cov}(Y_{ik}^{(t)}, Y_{il}^{(t)}) \\
&\dots + 2 \underbrace{\sum_{i=1}^{h^{(t)}}}_{i \neq a} \sum_{k=1}^{n_a^{(t)}} \sum_{l=1}^{n_i^{(t)}} \mathbf{Cov}(Y_{ak}^{(t)}, Y_{il}^{(t)}) \\
&\dots + 2 \underbrace{\sum_{i=1}^{h^{(t)}-1} \sum_{j=i+1}^{h^{(t)}}}_{i \neq j \neq a} \sum_{k=1}^{n_i^{(t)}} \sum_{l=1}^{n_j^{(t)}} \mathbf{Cov}(Y_{ik}^{(t)}, Y_{jl}^{(t)}) \\
&= n_a^{(t)} [\sigma_a^{(t)}]^2 + \underbrace{\sum_{i=1}^{h^{(t)}}}_{i \neq a} \{ n_{ai}^{-1} n_i^{(t)} (n_{ai} - 2) [\sigma_i^{(t)}]^2 + n_i^{(t)} \tau_i^2 \} + 0 \\
&\dots + \underbrace{\sum_{i=1}^{h^{(t)}}}_{i \neq a} \{ -2 n_{ai}^{-1} n_i^{(t)} (n_i^{(t)} - 1) [\sigma_i^{(t)}]^2 + n_i^{(t)} (n_i^{(t)} - 1) \tau_i^2 \} \\
&\dots + \underbrace{\sum_{i=1}^{h^{(t)}}}_{i \neq a} 2 n_{ai}^{-1} n_a^{(t)} n_i^{(t)} [\sigma_a^{(t)}]^2 \\
&\dots + \underbrace{\sum_{i=1}^{h^{(t)}} \sum_{j=i+1}^{h^{(t)}}}_{i \neq j \neq a} 2 n_{ai}^{-1} n_{aj}^{-1} n_i^{(t)} n_j^{(t)} \sum_{u \in S_{aij}} n_{aij}^{(u)} [\sigma_a^{(u)}]^2
\end{aligned}$$

$$\begin{aligned}
&= n_a^{(t)} \left(1 + 2 \sum_{\substack{i=1 \\ i \neq a}}^{h^{(t)}} n_{ai}^{-1} n_i^{(t)} \right) [\sigma_a^{(t)}]^2 \\
&\dots + \sum_{\substack{i=1 \\ i \neq a}}^{h^{(t)}} n_{ai}^{-1} n_i^{(t)} (n_{ai} - 2 n_i^{(t)}) [\sigma_a^{(t)}]^2 \\
&\dots + \sum_{\substack{i=1 \\ i \neq a}}^{h^{(t)}} [n_i^{(t)}]^2 \tau_i^2 \\
&\dots + \sum_{\substack{i=1 \\ i \neq j \neq a}}^{h^{(t)}-1} \sum_{j=i+1}^{h^{(t)}} 2 n_{ai}^{-1} n_{aj}^{-1} n_i^{(t)} n_j^{(t)} \sum_{u \in S_{aij}} n_{aij}^{(u)} [\sigma_a^{(u)}]^2
\end{aligned}$$

This result can be used for both the circumspect and retrospect estimators. In the latter case the batches only include the batch of interest and all relevant batches preceding that batch.

5 Estimating the Radiocarbon Age of a Sample

Given an appropriate estimate of the background activity with an associated error, it is now of interest to estimate the radiocarbon age of some sample. (For the rest of this section the term 'radiocarbon' will be dropped and the expression 'age of a sample' will be used where the context is understood.) It is presumed that several gross counts have been amassed for a number of oxalic standard samples and for some particular field sample. Given this data, how is the age of the sample to be estimated? This problem will be shown to be one of how to best combine all of the measurements made on the oxalic acid samples to produce a mean estimate of the standard activity.

5.1 A Quick Review

To suitably determine the age of a sample, we quickly review the statistical equation for the age of a sample. In section 1.5.2 an expression for the age of a sample was provided and is reproduced here for convenience:

$$t = \lambda^{-1} \log_e 0.95 \theta_s^{-1} \theta_{ox}$$

where

$$\theta_{ox} = \text{true oxalic standard activity}$$

$$\theta_s = \text{true field sample activity}$$

$$\lambda = \frac{\log_e 2}{t_{\frac{1}{2}}}$$

Deriving estimates for θ_{ox} and θ_s will provide an estimate for the age t of a sample. Deriving an estimate for θ_{ox} , the true standard activity, is the more interesting of the two. With several standard samples the problem is one of how to combine the various estimates of the standard activity to produce a mean estimate of the standard activity.

Before looking at this problem, however, we need to look at the data that we are working with. In particular, we need to examine the conversion from a single gross count measured on any standard or field sample to the normalised activity which is the data estimate of the true activity.

5.2 Converting the Gross Count to the Normalised Activity

To obtain the normalised activity we must make five adjustments to the gross count. Two adjustments are simple standardisations while the remaining three are compensations for factors which confound the true sample activity.

A description of each of these adjustments is given here :-

1. **standardisation for time** — the gross count is the total number of scintillations counted for the sample over a certain period of time. Since the counting time can vary according to the particular sample type — spiked samples can possess irregular counting times — it is necessary to standardise to counts per minute (cpm).
2. **standardisation for weight of sample benzene** — all sample solutions contain a fixed volume or weight of sample benzene. The entire content of benzene in the solution, however, is not necessarily indigenous to the sample and a certain amount may be a supplement of SGB used to top up to the optimal weight. This means

that the non-supplemented weight of sample benzene will vary and it is therefore necessary to standardise according to the weight of sample benzene since the number of scintillations recorded is directly proportional to that weight.

3. **compensation for background** — the true sample activity is unfortunately augmented and hence obscured by the background activity. This latter activity is an unavoidable nuisance factor which adds to the count rate of samples and must therefore be compensated for. The normal practice is to evaluate an independent estimate of background activity by counting some background samples. This estimate of background activity (expressed in cpm) is then subtracted in the estimation of the true sample activity.
4. **compensation for quenching** — the nature and problem of sample quenching has already been described in section 1.4.4. The existence of quenching will usually tend to deplete the observed sample count rate and so normally the sample quench factor is a multiplicative factor marginally greater than 1.
5. **compensation for fractionation** — the phenomenon of fractionation was discussed briefly in section 1.4.5. Like quenching, the fractionation effect will usually tend to deplete the observed sample count rate and so the fractionation factor is also a multiplicative factor which generally assumes a value marginally greater than 1.

All of the above adjustments can now be succinctly expressed by demonstrating the mathematical relationship between the gross count and the normalised activity:

$$A = (G/T - B) w^{-1} \cdot q \cdot f$$

where	A	=	normalised sample activity (cpm/g)
	G	=	sample gross count (c)
	T	=	sample counting time (m)
	B	=	background activity (cpm)
	w	=	weight of sample benzene (g)
	q	=	sample quench factor
	f	=	sample fractionation factor

This equation is the basis for adjusting all gross counts, pertaining to both standard and field samples, to normalised activities. The gross count over time denoted by G/T is the sample cpm value. The following definitions list the statistical parameters which are to replace the terms in the above equation.

5.3 Definitions

(D5.1) *gross counts over time — cpm values*

$$o_{ij} = j^{th} \text{ obsn. on } i^{th} \text{ standard sample, } i = 1, \dots, k, \quad j = 1, \dots, n_i$$

$$s_j = j^{th} \text{ obsn. on field sample, } j = 1, \dots, n_s$$

$$\hat{\mu}_b = \text{estimate of background activity}$$

(D5.2) *average values*

$$\bar{o}_i = \frac{1}{n_i} \sum_{j=1}^{n_i} o_{ij}, \quad i = 1, \dots, k$$

$$\bar{s} = \frac{1}{n_s} \sum_{j=1}^{n_s} s_j$$

(D5.3) *adjustments*

w_i = weight of sample benzene (g) in i^{th} standard sample

q_i = quench factor for i^{th} standard sample

f_i = fractionation factor for i^{th} standard sample

[substitute with w_s, q_s, f_s respectively for field sample]

5.4 Assumptions about Sample Observations

There are eight assumptions concerning sample observations that are presented here before proceeding to examine the problem of age estimation. These are :-

$$(A5.1) \text{Cov}(o_{ij}, o_{iq}) = 0, \quad \forall i, j, q, j \neq q$$

i.e. cpm values within standard samples are uncorrelated.

$$(A5.2) \text{Cov}(o_{ij}, o_{pq}) = 0, \quad \forall i, j, p, q, i \neq p$$

i.e. cpm values between standard samples are uncorrelated.

$$(A5.3) \text{Cov}(s_j, s_q) = 0, \quad \forall j, q, j \neq q$$

i.e. cpm values within field sample are uncorrelated.

$$(A5.4) \text{Cov}(o_{ij}, s_q) = 0, \quad \forall i, j, q$$

i.e. cpm values of standard samples and field sample are uncorrelated.

$$(A5.5) \text{Cov}(o_{ij}, \hat{\mu}_b) = 0, \forall i, j$$

i.e. cpm values of standard samples and background samples are uncorrelated.

$$(A5.6) \text{Cov}(s_j, \hat{\mu}_b) = 0, \forall j$$

i.e. cpm values of field sample and background samples are uncorrelated.

$$(A5.7) \text{Var}(o_{ij}) = \sigma_i^2, \forall i, j$$

i.e. standard sample cpm values have constant and unique variance within each sample.

$$(A5.8) \text{Var}(s_j) = \sigma_s^2, \forall j$$

i.e. field sample cpm values have constant variance.

The above assumptions underlie all methods of age estimation which appear in this report. These assumptions are considered to hold good for this present data due the small number of cycles in a batch. The size of the cycle fluctuations would not allow short-term trends to be detected over a mere 10 cycles. A longer counting series, however, might allow long-term trends to be detected. For example, Bowman et al. [10] have reported time trends appearing in data pertaining to modern standard samples between 1980 and 1984 at the British Museum. The cause of these trends has been attributed to evaporation losses. This problem is alleviated at East Kilbride through the flame sealing of sample vials. Although the method of age estimation developed in this work does not cater for time trends in the data, it might have general application once time trends are removed from the data. First, however, the conventional method of age estimation which was employed by the Glasgow laboratory before 1985 is examined.

5.5 Conventional Method of Age Estimation

The conventional method of age estimation which was originally used by the Glasgow laboratory is assessed before an alternative method is proposed. The method described here has been supplied by Dr. Gordon Cook although the notation is the author's.

This method presumes that the errors for weight of sample benzene and sample fractionation are so small that they can be considered to be zero, i.e. they are essentially treated as constants. The calculation of sample age and the calculation of error of age are presented separately. The major terms appearing in the calculations according to the laboratory method are distinguished by the use of the superscript 'c'. The terms are constructed from the previous definitions (D5.1)–(D5.3).

5.5.1 The Steps of the Calculation

(a) Calculation of Age

- *step 1 — sample estimates (accounting for background & weight of benzene)*

$$\psi_i = w_i^{-1} [\bar{o}_i - \hat{\mu}_b], \quad i = 1, \dots, k$$

$$\psi_s = w_s^{-1} [\bar{s} - \hat{\mu}_b]$$

- *step 2 — sample estimates (accounting for quenching & fractionation)*

$$\hat{\theta}_{\text{ox}i}^c = \psi_i \cdot q_i \cdot f_i, \quad i = 1, \dots, k$$

$$\hat{\theta}_s^c = \psi_s \cdot q_s \cdot f_s$$

- *step 3 — mean estimate of standard activity (unweighted average)*

$$\hat{\theta}_{\text{ox}}^c = \frac{1}{k} \sum_{i=1}^k \hat{\theta}_{\text{ox}_i}^c$$

- *step 4 — estimate of age*

$$\hat{t}^c = 8033 \log_e 0.95 [\hat{\theta}_s^c]^{-1} \hat{\theta}_{\text{ox}}^c$$

(b) *Calculation of Error of Age*

- *step 1 — errors (accounting for background & weight of benzene)*

$$\sigma(\psi_i) = \sigma(w_i^{-1} [\bar{o}_i - \hat{\mu}_b]) = w_i^{-1} \sqrt{\sigma^2(\bar{o}_i) + \sigma_b^2}, \quad i = 1, \dots, k$$

$$\sigma(\psi_s) = \sigma(w_s^{-1} [\bar{s} - \hat{\mu}_b]) = w_s^{-1} \sqrt{\sigma^2(\bar{s}) + \sigma_b^2}$$

- *step 2 — errors (accounting for quenching & fractionation)*

$$\sigma(\hat{\theta}_{\text{ox}_i}^c) = \hat{\theta}_{\text{ox}_i}^c \sqrt{\psi_i^{-2} \sigma^2(\psi_i) + q_i^{-2} \sigma^2(q_i)}, \quad i = 1, \dots, k$$

$$\sigma(\hat{\theta}_s^c) = \hat{\theta}_s^c \sqrt{\psi_s^{-2} \sigma^2(\psi_s) + q_s^{-2} \sigma^2(q_s)}$$

- *step 3 — error of mean estimate of standard activity*

$$\sigma(\hat{\theta}_{\text{ox}}^c) = \frac{1}{k} \sqrt{\sum_{i=1}^k \sigma^2(\hat{\theta}_{\text{ox}_i}^c)}$$

- *step 4 — error of age*

$$\sigma(\hat{t}^c) = 8033 \sqrt{[\hat{\theta}_{\text{ox}}^c]^{-2} \sigma^2(\hat{\theta}_{\text{ox}}^c) + [\hat{\theta}_s^c]^{-2} \sigma^2(\hat{\theta}_s^c)}$$

5.5.2 Assessment of the Conventional Method

The method which has just been outlined is adequate but not optimal. There are three main points to raise which each indicate a deficiency in the method.

The first point to raise concerning the conventional method is the use of an unweighted average for the mean standard activity. Even if the weights of sample benzene should be similar, significant differences in variability of the sample activities may occur. Indeed, in a later study it was observed that standard errors of sample activities pertaining to modern standard samples with similar weights of sample benzene demonstrated substantial differences. It is therefore better, in general, to seek a weighted average for the mean standard activity. (It must be stated that the laboratory has employed weighted averaging now for some time.)

The second point to make here is that the error of the age is not entirely correct — it is only an approximation. The reason that it is only an approximation is that the estimates for the activities of the standard samples are not independent as the method presumes. The estimates all contain a common correction for the background activity and this means that the estimates are not independent. It will be shown later in this section that this is of considerable importance.

The third and final point about the method is that it does not consider the possibility of sample bias. In the case of the background samples study, the samples were not all considered to be unbiased representatives of the true background activity. Similarly, there is always the possibility that standard samples may not all accurately reflect the true standard activity. A test for bias would be useful here and such a test is developed and presented in section 5.6.6.

All of the above points do not mean that the conventional estimate is a bad estimate. It

is the simplest estimate available and under stable conditions it should be quite adequate. The main argument, however, is that it is not optimal and a new approach to age estimation is sought here.

5.6 Alternative Approach to Age Estimation

The alternative approach to age estimation that is adopted here will be termed as *weighted least squares with covariances*. For convenience, this will be shortened to *weighted least squares* where it is understood that covariances are taken into account. The advantages of the method are :-

- (1) it produces a weighted average for the mean standard activity;
- (2) it does not treat the sample activities as independent;
- (3) it provides a test for bias among the standard samples.

Advantage (1) means greater robustness in the estimation of age, (2) means greater accuracy in the estimation of the error of age and (3) means more efficient screening of samples.

The method employed for estimating the mean standard activity is simply specialised to the case for a single sample in order to deal with the field sample. With respect to standard samples, it is of interest to develop a method of detecting bias among the samples. Before addressing the question of sample bias, however, we will look at the case which assumes no sample bias.

5.6.1 Modelling the Standard Activity (assuming no sample bias)

Let us now construct a model for the standard activity which assumes that there is no bias among the various standard samples. To do this it is necessary to introduce some more definitions. The new terms are constructed from the previous definitions (D5.1)–(D5.3).

(D5.4) *standard cpm values corrected for background*

$$o_{ij}^* = o_{ij} - \hat{\mu}_b, \quad i = 1, \dots, k, \quad j = 1, \dots, n_i$$

(D5.5) *adjustment factors (weight of benzene, quenching & fractionation)*

$$\gamma_i = w_i^{-1} \cdot q_i \cdot f_i, \quad i = 1, \dots, k$$

(D5.6) *normalised standard activities*

$$a_{ij} = \gamma_i \cdot o_{ij}^*, \quad i = 1, \dots, k, \quad j = 1, \dots, n_i$$

(D5.7) *average values*

$$\bar{a}_i = \frac{1}{n_i} \sum_{j=1}^{n_i} a_{ij} = \frac{1}{n_i} \sum_{j=1}^{n_i} \gamma_i \cdot o_{ij}^* = \gamma_i \cdot \bar{o}_i^*, \quad i = 1, \dots, k$$

Some assumptions are also made where \mathbf{E} is the expectation operator :-

$$(A5.9) \quad \mathbf{E}(a_{ij}) = \theta_{ox}, \quad \forall i, j$$

i.e. the expected value of the normalised standard activity is the true standard activity.

$$(A5.10) \quad \mathbf{E}(\gamma_i) = \Gamma_i, \quad \forall i$$

i.e. the expected value of the adjustment factor for any sample is some true underlying adjustment factor for that sample — this assumes that there is a true underlying quench factor for that sample since $\Gamma_i = \mathbf{E}(\gamma_i) = \mathbf{E}(w_i^{-1} \cdot q_i \cdot f_i) = w_i^{-1} \cdot f_i \cdot \mathbf{E}(q_i)$.

$$(A5.11) \quad \mathbf{Cov}(o_{ij}^*, \gamma_i) = 0, \quad \forall i, j$$

i.e. standard cpm values corrected for background are uncorrelated with adjustment factors.

$$(A5.12) \quad \mathbf{Cov}(\gamma_i, \gamma_j) = 0, \quad \forall i, j, i \neq j$$

i.e. adjustment factors are uncorrelated.

Using the above definitions and assumptions we have

$$\begin{aligned} \mathbf{E}(a_{ij}) &= \mathbf{E}(\gamma_i \cdot o_{ij}^*), \quad \forall i, j \\ \text{i.e.} \quad \theta_{ox} &= \Gamma_i \cdot \mathbf{E}(o_{ij}^*) \\ \text{i.e.} \quad \mathbf{E}(o_{ij}^*) &= \theta_{ox} \Gamma_i^{-1} \end{aligned}$$

This result leads to the proposal of a linear regression model which uses the observed adjustment factors as opposed to the expected adjustment factors:

$$\left. \begin{aligned} o_{ij}^* &= \theta_{ox} \gamma_i^{-1} + \epsilon_{ij} \quad \forall i, j \\ \text{where} \quad \mathbf{E}(\epsilon_{ij}) &= 0 \\ \mathbf{Var}(\epsilon_{ij}) &= \sigma_i^2 + \sigma_b^2 \\ \mathbf{Cov}(\epsilon_{ij}, \epsilon_{pq}) &= \sigma_b^2 \quad ij \neq pq \end{aligned} \right\} \quad (M5.1)$$

In the above model σ_i represents the standard error of the cpm values pertaining to the i th standard sample and σ_b represents the error of the estimate of the background activity. The justification for the proposed variances and covariances of the $\{\epsilon_{ij}\}$ is based on definition (D5.4) and on assumptions (A5.5) & (A5.7).

The model is not yet complete, however. To complete it we will introduce some vector and matrix definitions in order to simplify the proceedings.

5.6.2 Vector and Matrix Definitions

The terms that follow are constructed from previous definitions.

(D5.8) *vector of standard cpm values corrected for background*

$$\phi^T = \underbrace{(o_{11}^* \dots o_{1n_1}^* \vdots \dots \vdots o_{k1}^* \dots o_{kn_k}^*)}_{n=n_1+n_2+\dots+n_k}$$

(D5.9) *covariance matrix of ϕ*

$$\begin{aligned} V(\phi) &= \Sigma_\phi = M_{ox} + M_b \\ &= \text{diag}(\underbrace{\sigma_1^2 \dots \sigma_1^2}_{n_1} \vdots \dots \vdots \underbrace{\sigma_k^2 \dots \sigma_k^2}_{n_k}) + \sigma_b^2 \mathbf{1}_{n \times n} \\ &\quad \underbrace{\hspace{10em}}_{n=n_1+n_2+\dots+n_k} \end{aligned}$$

i.e. the $n \times n$ covariance matrix of ϕ where $\mathbf{1}_{n \times n}$ is the $n \times n$ matrix with each element equal to 1.

(D5.10) *vector of inverse adjustment factors*

$$\pi^T = \underbrace{(\underbrace{\gamma_1^{-1} \dots \gamma_1^{-1}}_{n_1} \vdots \dots \vdots \underbrace{\gamma_k^{-1} \dots \gamma_k^{-1}}_{n_k})}_{n=n_1+n_2+\dots+n_k}$$

(D5.11) *covariance matrix of π*

$$\mathbf{V}(\pi) = \Sigma_{\pi} = \underbrace{\begin{pmatrix} \tau_1^2 \mathbf{1}_{n_1 \times n_1} & \mathbf{0} & \cdots & \mathbf{0} \\ \mathbf{0} & \tau_2^2 \mathbf{1}_{n_2 \times n_2} & \cdots & \mathbf{0} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{0} & \mathbf{0} & \cdots & \tau_k^2 \mathbf{1}_{n_k \times n_k} \end{pmatrix}}_{n=n_1+n_2+\cdots+n_k}$$

i.e. the $n \times n$ covariance matrix of π where $\tau_i = \sigma(\gamma_i^{-1})$ the error of the inverse adjustment factor for the i th standard sample — the derivation of this matrix is from assumption (A5.12).

5.6.3 Re-expressing the Model

With the new vector and matrix notation we can transform model (M5.1) into a more compact definition:

$$\left. \begin{aligned} \mathbf{E}(\phi) &= \theta_{\text{ox}} \pi \\ \mathbf{V}(\phi) &= \Sigma_{\phi} \end{aligned} \right\} \quad (\text{M5.2})$$

To complete the model we make the final assumption that $\phi \sim \mathbf{N}(\theta_{\text{ox}} \pi, \Sigma_{\phi})$, i.e. the vector ϕ of sample cpm values corrected for background is multivariate normal. This is not just a convenient assumption chosen to make life easier. It is justified by the fact that the long counting times will tend to make standard and background sample observations reasonably normal. Earlier analysis of background samples (see section 2.2.2) has certainly showed that background sample observations conform reasonably well to the assumption of normality.

Using this model, the true standard activity θ_{ox} will now be estimated using weighted least squares.

5.6.4 Estimating the Standard Activity (assuming no sample bias)

In model (M5.2) above, the true standard activity θ_{ox} is the parameter of interest. To estimate this parameter we construct a suitable function of the terms $\{\theta_{\text{ox}}, \phi, \pi, \Sigma_\phi\}$ and θ_{ox} is estimated according to the appropriate weighted least squares estimator derived from this function. The function is based on model (M5.2):

$$S = S_{\phi, \pi, \Sigma_\phi}(\theta_{\text{ox}}) = (\phi - \theta_{\text{ox}} \pi)^T \Sigma_\phi^{-1} (\phi - \theta_{\text{ox}} \pi)$$

Expanding out the above equation we get

$$S = \phi^T \Sigma_\phi^{-1} \phi + \theta_{\text{ox}}^2 \pi^T \Sigma_\phi^{-1} \pi - 2 \theta_{\text{ox}} \pi^T \Sigma_\phi^{-1} \phi$$

The above function is minimised with respect to θ_{ox} by determining the derivative of S with respect to θ_{ox} and setting this derivative to zero. This yields an optimal estimator for the true standard activity θ_{ox} . It is optimal in the sense that it is minimum variance unbiased. (Only true if the covariance matrix is invertible which it is in this case.) The weighted least squares estimator — superscripted ‘ w ’ — is given by

$$\hat{\theta}_{\text{ox}}^w = (\pi^T \Sigma_\phi^{-1} \pi)^{-1} (\pi^T \Sigma_\phi^{-1} \phi) \quad (\text{E5.1})$$

and an approximate estimate of error for $\hat{\theta}_{\text{ox}}^w$ is

$$\left. \begin{aligned} \sigma(\hat{\theta}_{\text{ox}}^w) &\simeq \sqrt{(\pi^T \Sigma_\phi^{-1} \pi)^{-1} + (\pi^T \Sigma_\phi^{-1} \pi)^{-4} \lambda^T \Sigma_\pi \lambda} \\ \text{where } \lambda &= (\pi^T \Sigma_\phi^{-1} \pi) \Sigma_\phi^{-1} \phi - 2 (\pi^T \Sigma_\phi^{-1} \phi) \Sigma_\phi^{-1} \pi \end{aligned} \right\} \quad (\text{E5.2})$$

Equation (E5.1) is a standard result. Equation (E5.2) is less straightforward. The validation of (E5.2) is given in proof (P5.1) at the end of this section.

Parameters Σ_ϕ & Σ_π are unknown and have to be estimated from the data. An unbiased estimate for Σ_ϕ is easily produced. The $\{\sigma_i\}$ are simply replaced by $\{\hat{\sigma}_i\}$ where $\hat{\sigma}_i$ is the standard error of the cpm values of the i^{th} standard sample and σ_b is replaced by $\hat{\sigma}_b$ the standard error of the mean background activity. This gives $\hat{\Sigma}_\phi$ an unbiased estimate of Σ_ϕ . An estimate for Σ_π can also be produced although it is only an approximation. The $\{\tau_i\}$ are basically replaced by estimates $\{\hat{\tau}_i\}$ where the precise form of $\hat{\tau}_i$ is given in proposition (P5.2) at the end of the section. This gives us an estimate $\hat{\Sigma}_\pi$ of Σ_π .

5.6.5 Expanded Form of the Estimator

The form of $\hat{\theta}_{\text{ox}}^w$ given in equation (E5.1) is simply a weighted average of the standard sample activities. In fact, by expanding out the right-hand side of the equation it can be shown that

$$\hat{\theta}_{\text{ox}}^w = \left[\sum_{i=1}^k c_i \right]^{-1} \sum_{i=1}^k c_i \bar{a}_i.$$

where

$$c_i = n_i \gamma_i^{-2} \sigma_i^{-2} - n_i \gamma_i^{-1} \sigma_i^{-2} \left[\sum_{j=1}^k n_j \sigma_j^{-2} + \sigma_b^{-2} \right]^{-1} \left[\sum_{j=1}^k n_j \gamma_j^{-1} \sigma_j^{-2} \right]$$

The proof for this is given in (P5.3) at the end of the section. Since $\hat{\theta}_{\text{ox}}^w$ is minimum variance unbiased, it is the optimal weighted average that can be constructed for this data assuming that the model is valid. Its complex form is due to the correlation among observations. An examination of the terms c_i (the weights) in the expanded form of the estimator reveals that they are composed of the appropriate sample error minus a complex covariance term. If the covariance term is removed — this happens when the correlation among data is absent — then the result reduces to the familiar weighted average with only the sample variances appearing in the weights.

5.6.6 Modelling the Standard Activity (assuming sample bias)

Here we consider the possibility that bias is present among the standard samples. The weighted least squares estimate $\hat{\theta}_{\text{ox}}^w$, and indeed the conventional estimate $\hat{\theta}_{\text{ox}}^c$, will be affected by the presence of such bias.

If a significant degree of bias is present, then it is of interest to know if there is an

objective test that would verify the presence of such bias. It would also be of interest to know if there is an alternative estimator of θ_{ox} that would take into account the bias among samples.

The model that we use is

$$o_{ij}^* = (\theta_{\text{ox}} + \delta_i) \gamma_i^{-1} + \epsilon_{ij}, \quad \forall i, j \quad (\text{M5.3})$$

where all terms are defined as before in model (M5.1) with the new terms $\{\delta_i\}$ representing the biases of the standard samples. Expressing this in vector and matrix notation we obtain the concise model

$$\left. \begin{aligned} \mathbf{E}(\phi) &= \theta_{\text{ox}} \pi + \Upsilon_{\pi} \delta \\ \mathbf{V}(\phi) &= \Sigma_{\phi} \end{aligned} \right\} \quad (\text{M5.4})$$

where

$$\delta^T = (\delta_1 \ \delta_2 \ \cdots \ \delta_k)$$

$$\Upsilon_{\pi} = \begin{pmatrix} \gamma_1^{-1} & 0 & \cdots & 0 \\ \vdots & \vdots & & \vdots \\ \gamma_1^{-1} & 0 & \cdots & 0 \\ & \vdots & & \vdots \\ & 0 & 0 & \cdots \gamma_k^{-1} \\ & \vdots & \vdots & \vdots \\ & 0 & 0 & \cdots \gamma_k^{-1} \end{pmatrix} \begin{matrix} \uparrow \\ n_1 \\ \downarrow \\ \\ \uparrow \\ n_k \\ \downarrow \end{matrix}$$

$\underbrace{\hspace{10em}}_k$

with $\phi \sim N(\theta_{\text{ox}} \pi + \Upsilon_{\pi} \delta, \Sigma_{\phi})$, i.e. the vector ϕ is multivariate normal.

We construct a hypothesis test of the form

$$\text{H0 (null hypothesis)} : \delta = \mathbf{0}$$

$$\text{H1 (alternative)} : \delta \neq \mathbf{0}$$

where $\mathbf{0}$ is the zero vector. It is now of interest to see if we can construct a suitable test for the null hypothesis. To do this we construct an appropriate least squares function as before but this time we take the bias into account. The function that we use is based on model (M5.4) above:

$$S^* = S_{\phi, \pi, \Upsilon_\pi, \Sigma_\phi}^*(\theta_{\text{ox}}, \delta) = (\phi - \theta_{\text{ox}} \pi - \Upsilon_\pi \delta)^T \Sigma_\phi^{-1} (\phi - \theta_{\text{ox}} \pi - \Upsilon_\pi \delta)$$

Using this function we can derive estimates of θ_{ox} and δ under both the null hypothesis and the alternative hypothesis. Taking the simpler hypothesis of the two, namely the null hypothesis, we note that if δ is taken to be $\mathbf{0}$ then S^* reduces to S as in section 5.6.1. This means that the best estimator of θ_{ox} under H0, which we will denote by $\hat{\theta}_{\text{ox}}^{\text{h0}}$, is simply $\hat{\theta}_{\text{ox}}^w$ which was presented in section 5.6.1. The estimates for θ_{ox} and δ under the null hypothesis are therefore

$$\left. \begin{aligned} \hat{\theta}_{\text{ox}}^{\text{h0}} &= (\pi^T \Sigma_\phi^{-1} \pi)^{-1} (\pi^T \Sigma_\phi^{-1} \phi) \\ \hat{\delta}^{\text{h0}} &= \mathbf{0} \end{aligned} \right\} \quad (\text{E5.5})$$

If the alternative hypothesis is true, however, then we must look at the derivatives of S^* with respect to both θ_{ox} and δ to derive estimators for them. Accordingly, the alternative hypothesis yields the estimators

$$\left. \begin{aligned}
\hat{\theta}_{\text{ox}}^{\text{h1}} &= (\pi^T \Omega \pi)^{-1} (\pi^T \Omega \phi) \\
\hat{\delta}^{\text{h1}} &= \Lambda \phi - (\pi^T \Omega \pi)^{-1} (\pi^T \Omega \phi) \Lambda \pi \\
\text{where } \Lambda &= (\Upsilon_{\pi}^T \Sigma_{\phi}^{-1} \Upsilon_{\pi})^{-1} \Upsilon_{\pi}^T \Sigma_{\phi}^{-1} \\
\text{and } \Omega &= \Sigma_{\phi}^{-1} - \Sigma_{\phi}^{-1} \Upsilon_{\pi} (\Upsilon_{\pi}^T \Sigma_{\phi}^{-1} \Upsilon_{\pi})^{-1} \Upsilon_{\pi}^T \Sigma_{\phi}^{-1}
\end{aligned} \right\} \quad (\text{E5.6})$$

Validation of these estimators is given in proof (P5.4) and their property of unbiasedness is presented in proposition (P5.5). The covariance matrix Σ_{ϕ} must be estimated. This means that we must replace Σ_{ϕ} by $\hat{\Sigma}_{\phi}$ as before.

Due to the assumption of the vector ϕ being multivariate normal, we have that

$$S_{\phi, \pi, \Upsilon_{\pi}, \Sigma_{\phi}}^*(\hat{\theta}_{\text{ox}}^{\text{h0}}, \hat{\delta}^{\text{h0}}) \sim \chi^2(n - k - 1)$$

$$S_{\phi, \pi, \Upsilon_{\pi}, \Sigma_{\phi}}^*(\hat{\theta}_{\text{ox}}^{\text{h1}}, \hat{\delta}^{\text{h1}}) \sim \chi^2(n - 2k - 1)$$

The degrees of freedom are calculated in H0 as n observations minus 1 estimated parameter $\hat{\theta}_{\text{ox}}^{\text{h0}}$ and in H1 as n observations minus k estimated parameters $\{\hat{\delta}_i^{\text{h1}}\}$ and 1 estimated parameter $\hat{\theta}_{\text{ox}}^{\text{h1}}$. Since Σ_{ϕ} is unknown it is necessary to remove a further k degrees of freedom from each of the chi-squared distributions. This loss of k degrees of freedom is due to the estimation of the k parameters $\{\sigma_i\}$ in Σ_{ϕ} . (There is no loss of freedom for σ_b since an estimate for this is derived independently.)

The appropriate test here is to perform the standard F-test of the null hypothesis versus the alternative hypothesis. This test will determine if there is significant bias among the standard samples or not. If the test proves positive, then bias is present but it will not indicate which samples are biased and which are not. This has to be determined separately and depends on the $\{\hat{\delta}_i^{\text{h1}}\}$ values. Larger values indicate larger departures from some average sample activity. It would be a simple matter to observe the case of a single sample giving rise

rise to bias — its $\hat{\delta}_i^{h1}$ value will depart significantly from the values of other samples, the latter being clustered together. In such a case the evidence might prompt the analyst to remove the outlying sample from the calculation of the mean standard activity. Another approach might be to consider it to be an unaligned sample and make some data corrections in a similar manner to that which has been outlined for background samples in section 4.2. On the other hand, if all $\{\hat{\delta}_i^{h1}\}$ values are dissimilar and wide apart, then the analyst is faced with the problem of diverging sample activities. In that case it would not be clear what the standard sample activities would each be representing.

For the remaining part of this study it is assumed that bias is not present or has been suitably dealt with subsequent to detection. The above test is the recommended statistical means for such detection.

5.6.7 Estimating the Activities of Field Samples

To estimate the activity of the field sample, it is a simple matter of specialising the case for the standard samples to the case for a single sample. This means that equations (E5.1) and (E5.2) still hold good for a single sample. If we take ϕ_s to be the vector of field sample cpm values corrected for background and take γ_s to be the adjustment factor for the sample, then plugging these terms into equations (E5.1) and (E5.2) we have

$$\left. \begin{aligned} \hat{\theta}_s^w &= \gamma_s (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1})^{-1} (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \phi_s) \\ \sigma(\hat{\theta}_s^w) &\simeq \sqrt{\gamma_s^2 (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1})^{-1} + \gamma_s^4 \tau_s^2 (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1})^{-4} (\mathbf{1}^T \lambda_s)^2} \\ \lambda_s &= (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1}) \Sigma_{\phi_s}^{-1} \phi_s - 2 (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \phi_s) \Sigma_{\phi_s}^{-1} \mathbf{1} \end{aligned} \right\} \quad (\text{E5.7})$$

where $\mathbf{1}$ is the $n_s \times 1$ unit vector, $\mathbf{1}_{n_s \times n_s}$ is the square unit matrix of the indicated dimensions and τ_s is the error of the inverse adjustment factor for the sample. By expanding out the terms in (E5.7) it can be shown that $\hat{\theta}_s^w = \bar{a}_s$, the average normalised field sample activity and $\sigma(\hat{\theta}_s^w) = \sigma(\bar{a}_s)$. These results are verified in proof (P5.6). Thus equations (E5.1) and (E5.2) provide a weighted average of sample averages in the general case and in the case of a single sample it reduces naturally to the sample average itself.

5.6.8 Calculating the Age of a Sample

The final step is to calculate the age of some sample. The estimator for the age is simply

$$\hat{t}^w = \lambda^{-1} \log_e 0.95 [\hat{\theta}_s^w]^{-1} \hat{\theta}_{\text{ox}}^w \quad (\text{E5.8})$$

It is normally assumed that $\lambda^{-1} = 8033$. It is also assumed under stable conditions that the two age estimators, conventional and weighted least squares, would not be dramatically different but the weighted least squares estimator offers a greater robustness under a broader range of conditions. For instance, standard samples with relatively larger variability will be 'played down' in the weighted average approach. (Larger variability may indicate less reliability.)

The error for the weighted least squares estimator of age does not assume independence between standard sample cpm values corrected for background and field sample cpm values corrected for background. This is to maintain consistency since standard sample cpm values corrected for background are not treated as independent data. With this in mind it can be shown that

$$\left. \begin{aligned} \sigma(\hat{t}^w) &\simeq 8033 \times \left[[\hat{\theta}_{ox}^w]^{-2} \sigma^2(\hat{\theta}_{ox}^w) + [\hat{\theta}_s^w]^{-2} \sigma^2(\hat{\theta}_s^w) \right. \\ &\quad \left. \dots - 2 [\hat{\theta}_{ox}^w]^{-1} [\hat{\theta}_s^w]^{-1} \text{Cov}(\hat{\theta}_{ox}^w, \hat{\theta}_s^w) \right]^{\frac{1}{2}} \\ \text{Cov}(\hat{\theta}_{ox}^w, \hat{\theta}_s^w) &= \sigma_b^2 \gamma_s (\pi^T \Sigma_\phi^{-1} \pi)^{-1} (\pi^T \Sigma_\phi^{-1} \mathbf{1}) \end{aligned} \right\} \quad (\text{E5.9})$$

This error is verified in proof (P5.7). The task of producing estimates of ages and corresponding errors, using the estimators defined in (E5.8) and (E5.9) respectively, is made relatively easy with the computer.

5.6.9 Data Application

It is now worthwhile to look at the two age estimators applied to some actual data. The data is supplied by Dr. Cook and was collected over a period of four months from 3/4/84 to 24/7/84. This data is more recent than the data analysed in previous sections. To assess the two methods of age estimation, two field samples are selected from each of the eight batches that pertain to this time interval. These samples cover a broad range of sample dates.

The analysis here is not intended to ascertain which of the two estimators is more accurate. This cannot be established since the true radiocarbon ages of the various samples are not known. Only a simulation study can shed some light on this matter (see section 6).

Batch	Sample	\hat{t}^c (a)	$\hat{\sigma}(\hat{t}^c)$ (b)	\hat{t}^w (c)	$\hat{\sigma}(\hat{t}^w)$ (d)	Estimate Differences (c) - (a)	% Error Differences [(d) - (b)]/(b) \times 100%
1	GU-1761	5441	235	5449	215	+8	-8.5%
	GU-1730	3278	148	3287	140	+9	-5.4%
2	GU-1729	6734	174	6714	160	-20	-8.0%
	GU-1724	161	81	141	70	-20	-13.6%
3	GU-1709	4777	299	4758	277	-19	-7.4%
	GU-1762	7850	375	7831	353	-19	-5.9%
4	GU-1731	3560	106	3596	94	+36	-11.3%
	GU-1732	6123	159	6159	148	+36	-6.9%
5	GU-1733	1644	128	1633	121	-11	-5.5%
	GU-1734	4630	107	4619	92	-11	-14.0%
6	GU-1735	2513	93	2523	85	+10	-8.6%
	GU-1736	2251	122	2260	111	+9	-8.3%
7	GU-1785	6010	211	6006	191	-4	-9.5%
	GU-1779	3981	276	3976	255	-5	-7.6%
8	GU-1781	1575	151	1578	139	+3	-7.9%
	GU-1782	1431	232	1434	216	+3	-6.9%

Table 10: the estimates of sample ages using the conventional and weighted least squares methods (c and w respectively).

What is sought here is a simple comparison of the two estimators in order to see if there is any pattern between them. For instance, do they produce consistently different estimates? Are the errors of the two types of estimates different?

The results of this analysis are presented in Table 10. Several conclusions can be drawn :-

- (1) There is no substantial difference between the two estimators in terms of point estimates. The largest differences of around 40 years for the two samples recorded in batch 4 are not massive considering the calculated ages of the samples. An average absolute difference of 13.9 years is measured between the two estimators for this data.
- (2) Differences between the two estimators appear to be constant in any single batch,

i.e. pairs of samples in each batch produce virtually identical differences. Differences also do not appear to be correlated with the ages of samples. This must be the case since $\hat{\theta}_s^w = \hat{\theta}_s^c = \bar{a}_s$. This fact means that

$$\hat{t}^w - \hat{t}^c = \lambda^{-1} \log_e [\hat{\theta}_{ox}^c]^{-1} \hat{\theta}_{ox}^w$$

In other words, differences between the two age estimators in a single batch are not dependent upon the activities (and hence the ages) of field samples contained in that batch but rather upon the difference between the two estimates of mean standard activity for that batch. This is why the differences are constant in any single batch and why the differences appear to be uncorrelated with the ages of samples. (The fact that the differences are sometimes 'out' by about 1 year in any batch is probably due to rounding errors.)

- (3) Errors for the estimates pertaining to the two estimators are appreciably different.

The errors associated with the weighted least squares method are an improvement on the errors associated with the conventional method. On average the relative error reduction is 8.5%. This is substantial and if we consider that a field sample is measured over several batches from which a pooled estimate of age is derived, then this advantage becomes increasingly profitable. An explanation for this reduction in error is that the weighted least squares method accounts for correlation among the observations and this leads to a more precise and narrower estimate of error. Proof of this can be found in Table 11 which presents the errors for weighted least square estimates assuming no correlation among observations. As can be seen, the errors

Batch	Sample	$\hat{\sigma}(\hat{t}^c)$	$\hat{\sigma}(\hat{t}^{w0})$	$\hat{\sigma}(\hat{t}^w)$
1	GU-1761	235	234	215
	GU-1730	148	146	140
2	GU-1729	174	173	160
	GU-1724	81	78	70
3	GU-1709	299	298	277
	GU-1762	375	374	353
4	GU-1731	106	103	94
	GU-1732	159	158	148
5	GU-1733	128	127	121
	GU-1734	107	106	92
6	GU-1735	93	92	85
	GU-1736	122	121	111
7	GU-1785	211	210	191
	GU-1779	276	275	255
8	GU-1781	151	150	139
	GU-1782	232	232	216

Table 11: errors for conventional 'c', weighted least squares with zero covariances 'w0' and weighted least squares with non-zero covariances 'w'.

for the conventional estimates are virtually identical with the errors for weighted least squares estimates assuming no correlation. This suggests that if a true error was formulated for the conventional estimator, then conventional errors would be more compatible with the errors recorded for weighted least squares with non-zero covariances.

The advantage of the weighted least squares approach can be understood as being an advantage which is gained over two main features of the data. The first is the size of the mean background error. The measure of gain in using weighted least squares is clearly related to the size of this error. The larger the mean background error is, the larger the covariances among the background corrected data will be. Also, the gain factor is clearly dependent on the number of data, that is, upon the size of the counting series. The longer

series, the greater the gain will be. This just leaves us to assess the conventional and weighted least squares estimators via a suitable simulation study.

5.7 Proofs and Propositions

Proof (P5.1) for error equation (E5.2)

- *proof for:*

$$\sigma(\hat{\theta}_{\text{ox}}^w) \simeq \sqrt{(\pi^T \Sigma_\phi^{-1} \pi)^{-1} + (\pi^T \Sigma_\phi^{-1} \pi)^{-4} \lambda^T \Sigma_\pi \lambda}$$

$$\text{where} \quad \lambda = (\pi^T \Sigma_\phi^{-1} \pi) \Sigma_\phi^{-1} \phi - 2(\pi^T \Sigma_\phi^{-1} \phi) \Sigma_\phi^{-1} \pi$$

Let us define the vector

$$\alpha^T = (\phi^T \mid \pi^T)$$

to be the combined vector of the standard sample cpm values corrected for background and the inverse adjustment factors corresponding to those values. Then, according to assumption (A5.11), the covariance matrix for α is

$$\Sigma_\alpha = \begin{pmatrix} \Sigma_\phi & \mathbf{0} \\ \mathbf{0} & \Sigma_\pi \end{pmatrix}$$

Essentially we are interested in the estimator $\hat{\theta}_{\text{ox}}^w$ which is a function of the vector α .

This can be expressed

$$f(\alpha) = \hat{\theta}_{\text{ox}}^w = (\pi^T \Sigma_\phi^{-1} \pi)^{-1} (\pi^T \Sigma_\phi^{-1} \phi) = v^{-1} u \quad \text{say.}$$

Let $\mathbf{d}f$ denote the vector of derivatives of the function f with respect to both ϕ and π . This gives us the vector

$$\begin{aligned}
\mathbf{d}f &= \begin{pmatrix} \frac{df}{d\phi} \\ \frac{df}{d\pi} \end{pmatrix} \\
&= \begin{pmatrix} (\pi^T \Sigma_\phi^{-1} \pi)^{-1} \Sigma_\phi^{-1} \pi \\ (\pi^T \Sigma_\phi^{-1} \pi)^{-2} [(\pi^T \Sigma_\phi^{-1} \pi) \Sigma_\phi^{-1} \phi - 2(\pi^T \Sigma_\phi^{-1} \pi) \Sigma_\phi^{-1} \pi] \end{pmatrix} \\
&= \begin{pmatrix} v^{-1} \Sigma_\phi^{-1} \pi \\ v^{-2} [v \Sigma_\phi^{-1} \phi - 2u \Sigma_\phi^{-1} \pi] \end{pmatrix}
\end{aligned}$$

Using a standard approximation for the error and noting from their definitions that the matrices Σ_ϕ and Σ_π are symmetrical, we finally have that

$$\begin{aligned}
\sigma(\hat{\theta}_{\text{ox}}^w) &\simeq [\mathbf{d}f^T \Sigma_\alpha \mathbf{d}f]^{\frac{1}{2}} \\
&= \sqrt{v^{-2} \pi^T \Sigma_\phi^{-1} \Sigma_\phi \Sigma_\phi^{-1} \pi + v^{-4} \lambda^T \Sigma_\pi \lambda}, \quad \lambda = v \Sigma_\phi^{-1} \phi - 2u \Sigma_\phi^{-1} \pi \\
&= \sqrt{v^{-1} + v^{-4} \lambda^T \Sigma_\pi \lambda} \\
&= \sqrt{(\pi^T \Sigma_\phi^{-1} \pi)^{-1} + (\pi^T \Sigma_\phi^{-1} \pi)^{-4} \lambda^T \Sigma_\pi \lambda}
\end{aligned}$$

This completes the result.

Proposition (P5.2) for the Form of τ (error of inverse adjustment factor)

• *proposition is:*

$$\tau \simeq \gamma^{-1} q^{-1} \sigma(q)$$

where q is the unknown quench factor for some standard or field sample. The proof for this is fairly straightforward:

$$\gamma^{-1} = w f^{-1} q^{-1} \quad \text{by definition (D5.5)}$$

$$\text{And so} \quad \tau = w f^{-1} \sigma(q^{-1})$$

$$\text{Now let} \quad f(q) = q^{-1}$$

$$\text{Then} \quad \frac{df}{dq} = -q^{-2}$$

$$\begin{aligned} \text{Thus} \quad \tau &\simeq w f^{-1} \left[\sigma(q) \times \frac{df}{dq} \right] \\ &= w f^{-1} q^{-2} \sigma(q) \\ &= \gamma^{-1} q^{-1} \sigma(q) \end{aligned}$$

This is the appropriate form for the error τ of the inverse adjustment factor and details of the estimation of $\sigma(q)$ appear in section 7.2.1.

Proof (P5.3) for Expanded Form of $\hat{\theta}_{\text{ox}}^w$

• *proof for:*

$$\hat{\theta}_{\text{ox}}^w = \left[\sum_{i=1}^k c_i \right]^{-1} \sum_{i=1}^k c_i \bar{a}_i.$$

where

$$c_i = n_i \gamma_i^{-2} \sigma_i^{-2} - n_i \gamma_i^{-1} \sigma_i^{-2} \left[\sum_{j=1}^k n_j \sigma_j^{-2} + \sigma_b^{-2} \right]^{-1} \left[\sum_{j=1}^k n_j \gamma_j^{-1} \sigma_j^{-2} \right]$$

The proof for this is in four parts :-

(a) *By definition (D5.9) —*

$$\Sigma_\phi = M_{\text{ox}} + \sigma_b^2 \mathbf{1}_n \mathbf{1}_n^T$$

$$\text{i.e. } \Sigma_\phi^{-1} = M_{\text{ox}}^{-1} - z^{-1} M_{\text{ox}}^{-1} \mathbf{1}_n \mathbf{1}_n^T M_{\text{ox}}^{-1}, \quad z = \sum_{j=1}^k n_j \sigma_j^{-2} + \sigma_b^{-2}$$

(b) *There are four basic results —*

1. $\mathbf{1}_n^T M_{\text{ox}}^{-1} \pi = \sum_{i=1}^k n_i \sigma_i^{-2} \gamma_i^{-1}$
2. $\mathbf{1}_n^T M_{\text{ox}}^{-1} \phi = \sum_{i=1}^k n_i \sigma_i^{-2} \gamma_i^{-1} \bar{a}_i.$
3. $\pi^T M_{\text{ox}}^{-1} \pi = \sum_{i=1}^k n_i \sigma_i^{-2} \gamma_i^{-2}$
4. $\pi^T M_{\text{ox}}^{-1} \phi = \sum_{i=1}^k n_i \sigma_i^{-2} \gamma_i^{-2} \bar{a}_i.$

(c) *Using the results in (b) we obtain —*

$$\begin{aligned}
 \pi^T \Sigma_{\phi}^{-1} \phi &= \pi^T M_{\text{ox}}^{-1} \phi - z^{-1} (\mathbf{1}_n^T M_{\text{ox}}^{-1} \pi) \mathbf{1}_n^T M_{\text{ox}}^{-1} \phi \\
 &= \sum_{i=1}^k n_i \sigma_i^{-2} \gamma_i^{-2} \bar{a}_i. \\
 &\quad \dots - z^{-1} (\sum_{i=1}^k n_i \sigma_i^{-2} \gamma_i^{-1}) \sum_{i=1}^k n_i \sigma_i^{-2} \gamma_i^{-1} \bar{a}_i. \\
 &= \sum_{i=1}^k [n_i \sigma_i^{-2} \gamma_i^{-2} - n_i \sigma_i^{-2} \gamma_i^{-1} z^{-1} (\sum_{i=1}^k n_i \sigma_i^{-2} \gamma_i^{-1})] \bar{a}_i.
 \end{aligned}$$

(d) *Using the results in (b) we also obtain —*

$$\begin{aligned}
 \pi^T \Sigma_{\phi}^{-1} \pi &= \pi^T M_{\text{ox}}^{-1} \pi - z^{-1} (\mathbf{1}_n^T M_{\text{ox}}^{-1} \pi)^2 \\
 &= \sum_{i=1}^k [n_i \sigma_i^{-2} \gamma_i^{-2} - n_i \sigma_i^{-2} \gamma_i^{-1} z^{-1} (\sum_{i=1}^k n_i \sigma_i^{-2} \gamma_i^{-1})]
 \end{aligned}$$

The proof now follows from the definition of $\hat{\theta}_{\text{ox}}^w$ and results (c) and (d).

Proof (P5.4) for the Form of Estimators Under the Alternative Hypothesis

• *proof for:*

$$\left. \begin{aligned} \hat{\theta}_{\text{ox}}^{\text{h1}} &= (\pi^{\text{T}} \Omega \pi)^{-1} (\pi^{\text{T}} \Omega \phi) \\ \hat{\delta}^{\text{h1}} &= \Lambda \phi - (\pi^{\text{T}} \Omega \pi)^{-1} (\pi^{\text{T}} \Omega \phi) \Lambda \pi \end{aligned} \right\}$$

where $\Lambda = (\Upsilon_{\pi}^{\text{T}} \Sigma_{\phi}^{-1} \Upsilon_{\pi})^{-1} \Upsilon_{\pi}^{\text{T}} \Sigma_{\phi}^{-1}$

and $\Omega = \Sigma_{\phi}^{-1} - \Sigma_{\phi}^{-1} \Upsilon_{\pi} (\Upsilon_{\pi}^{\text{T}} \Sigma_{\phi}^{-1} \Upsilon_{\pi})^{-1} \Upsilon_{\pi}^{\text{T}} \Sigma_{\phi}^{-1}$

These results are verified by looking at the sum of squares function that corresponds to the model under the alternative hypothesis. This function is

$$S^* = (\phi - \theta_{\text{ox}} \pi - \Upsilon_{\pi} \delta)^{\text{T}} \Sigma_{\phi}^{-1} (\phi - \theta_{\text{ox}} \pi - \Upsilon_{\pi} \delta)$$

From this function we have that

$$\frac{\text{d}S^*}{\text{d}\delta} = -\Upsilon_{\pi}^{\text{T}} \Sigma_{\phi}^{-1} \Upsilon_{\pi} \delta + \Upsilon_{\pi}^{\text{T}} \Sigma_{\phi}^{-1} \phi - \theta_{\text{ox}} \Upsilon_{\pi}^{\text{T}} \Sigma_{\phi}^{-1} \pi$$

Then

$$\begin{aligned} \bar{\delta}^{\text{h1}} &= \{ \delta : \frac{\text{d}S^*}{\text{d}\delta} = 0 \} \\ &= \Lambda (\phi - \theta_{\text{ox}} \pi), \quad \Lambda = (\Upsilon_{\pi}^{\text{T}} \Sigma_{\phi}^{-1} \Upsilon_{\pi})^{-1} \Upsilon_{\pi}^{\text{T}} \Sigma_{\phi}^{-1} \end{aligned}$$

Thus

$$\begin{aligned} \frac{\text{d}S^*}{\text{d}\theta_{\text{ox}}} \big|_{\delta=\bar{\delta}^{\text{h1}}} &= -\theta_{\text{ox}} \pi^{\text{T}} \Sigma_{\phi}^{-1} \pi + \theta_{\text{ox}} \pi^{\text{T}} \Lambda^{\text{T}} \Upsilon_{\pi}^{\text{T}} \Sigma_{\phi}^{-1} \pi \\ &\quad \dots + \pi^{\text{T}} \Sigma_{\phi}^{-1} \phi - \pi^{\text{T}} \Lambda^{\text{T}} \Upsilon_{\pi}^{\text{T}} \Sigma_{\phi}^{-1} \phi \end{aligned}$$

This gives
$$\hat{\theta}_{\text{ox}}^{\text{h1}} = (\pi^T \Omega \pi)^{-1} (\pi^T \Omega \phi), \quad \Omega = \Sigma_{\phi}^{-1} - \Lambda^T \Upsilon_{\pi}^T \Sigma_{\phi}^{-1}$$

and
$$\begin{aligned} \hat{\delta}^{\text{h1}} &= \tilde{\delta}^{\text{h1}} \mid_{\theta_{\text{ox}} = \hat{\theta}_{\text{ox}}^{\text{h1}}} \\ &= \Lambda \phi - (\pi^T \Omega \pi)^{-1} (\pi^T \Omega \phi) \Lambda \pi \end{aligned}$$

Hence result.

Proposition (P5.5) about Unbiasedness of $\hat{\theta}_{\text{ox}}^{\text{h1}}$ and $\hat{\delta}^{\text{h1}}$

• *proposition is:*

$$\left. \begin{aligned} \mathbf{E}(\hat{\theta}_{\text{ox}}^{\text{h1}} \mid \text{H1 is true}) &= \theta_{\text{ox}} \\ \mathbf{E}(\hat{\delta}^{\text{h1}} \mid \text{H1 is true}) &= \delta \end{aligned} \right\}$$

The proofs are :-

$$\begin{aligned} (1) \quad \mathbf{E}(\hat{\theta}_{\text{ox}}^{\text{h1}} \mid \text{H1 is true}) &= \mathbf{E}[(\pi^T \Omega \pi)^{-1} (\pi^T \Omega \phi)] \\ &= (\pi^T \Omega \pi)^{-1} \pi^T \Omega (\theta_{\text{ox}} \pi + \Upsilon_{\pi} \delta) \\ &= \theta_{\text{ox}} + (\pi^T \Omega \pi)^{-1} \pi^T \Omega \Upsilon_{\pi} \delta \\ &= \theta_{\text{ox}} \end{aligned}$$

This result is due to the fact that

$$\begin{aligned} \Omega \Upsilon_{\pi} &= \Sigma_{\phi}^{-1} \Upsilon_{\pi} - \Sigma_{\phi}^{-1} \Upsilon_{\pi} (\Upsilon_{\pi}^T \Sigma_{\phi}^{-1} \Upsilon_{\pi})^{-1} \Upsilon_{\pi}^T \Sigma_{\phi}^{-1} \Upsilon_{\pi} \\ &= \Sigma_{\phi}^{-1} \Upsilon_{\pi} - \Sigma_{\phi}^{-1} \Upsilon_{\pi} \\ &= \mathbf{0} \end{aligned}$$

$$\begin{aligned}
 (2) \quad \mathbf{E}(\hat{\delta}^{\text{hl}} \mid H1 \text{ is true}) &= \mathbf{E}[\Lambda(\phi - \hat{\theta}_{\text{ox}}^{\text{hl}} \pi)] \\
 &= \Lambda(\theta_{\text{ox}} \pi + \Upsilon_{\pi} \delta - \theta_{\text{ox}} \pi) \\
 &= \Lambda \Upsilon_{\pi} \delta \\
 &= \delta
 \end{aligned}$$

$$\begin{aligned}
 \text{Since} \quad \Lambda \Upsilon_{\pi} &= (\Upsilon_{\pi}^T \Sigma_{\phi}^{-1} \Upsilon_{\pi})^{-1} \Upsilon_{\pi}^T \Sigma_{\phi}^{-1} \Upsilon_{\pi} \\
 &= \mathbf{I}, \quad \text{the identity matrix}
 \end{aligned}$$

Proof (P5.6) Concerning Estimate of Field Sample Activity

• *proof for:*

$$\left. \begin{aligned} \hat{\theta}_s^w &= \bar{a}_s. \\ \sigma(\hat{\theta}_s^w) &= \sigma(\bar{a}_s.) \end{aligned} \right\}$$

(1) Proof for $\hat{\theta}_s^w = \bar{a}_s$.

The proof requires some definitions to be given first :-

- i. $s_j = j^{\text{th}}$ sample cpm value
- ii. $s_j^* = s_j - \hat{\mu}_b$
- iii. $s_s^* = \sum_{j=1}^{n_s} s_j^*$
- iv. $\sigma_s = \sigma(s_j)$

Using the preceding definitions we have

$$\begin{aligned}
v_s &= \gamma_s^{-2} \mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1} \\
&= \gamma_s^{-2} \mathbf{1}^T [\sigma_s^{-2} \mathbf{I} - z^{-1} \sigma_s^{-4} \mathbf{1} \mathbf{1}^T] \mathbf{1}, & z &= n_s \sigma_s^{-2} + \sigma_b^{-2} \\
&= \gamma_s^{-2} [\sigma_s^{-2} \mathbf{1}^T \mathbf{1} - z^{-1} \sigma_s^{-4} (\mathbf{1}^T \mathbf{1})^2] \\
&= \gamma_s^{-2} [n_s \sigma_s^{-2} - z^{-1} n_s^2 \sigma_s^{-4}] \\
&= \gamma_s^{-2} n_s z^{-1} \sigma_s^{-2} [z - n_s \sigma_s^{-2}] \\
&= \gamma_s^{-2} n_s z^{-1} \sigma_s^{-2} \sigma_b^{-2} \\
&= \gamma_s^{-2} n_s [z \sigma_s^2 \sigma_b^2]^{-1} \\
&= \gamma_s^{-2} n_s [n_s \sigma_b^2 + \sigma_s^2]^{-1} \\
&= \gamma_s^{-2} [n_s^{-1} \sigma_s^2 + \sigma_b^2]^{-1} \\
\\
u_s &= \gamma_s^{-1} \mathbf{1}^T \Sigma_{\phi_s}^{-1} \phi_s \\
&= \gamma_s^{-1} \mathbf{1}^T [\sigma_s^{-2} \mathbf{I} - z^{-1} \sigma_s^{-4} \mathbf{1} \mathbf{1}^T] \phi_s \\
&= \gamma_s^{-1} [\sigma_s^{-2} (\mathbf{1}^T \phi_s) - z^{-1} n_s \sigma_s^{-4} (\mathbf{1}^T \phi_s)] \\
&= \gamma_s^{-1} [\gamma_s^{-1} n_s \sigma_s^{-2} \bar{a}_s - z^{-1} \gamma_s^{-1} n_s^2 \sigma_s^{-4} \bar{a}_s] \\
&= \gamma_s^{-2} [n_s \sigma_s^{-2} - z^{-1} n_s^2 \sigma_s^{-4}] \bar{a}_s \\
&= v_s \bar{a}_s. & (\text{see line 4 of equation for } v_s \text{ above})
\end{aligned}$$

From these equations we finally obtain the result

$$\hat{\theta}_s^w = \gamma_s (\mathbf{1} \Sigma_{\phi_s}^{-1} \mathbf{1})^{-1} (\mathbf{1} \Sigma_{\phi_s}^{-1} \phi_s) = v_s^{-1} u_s = v_s^{-1} v_s \bar{a}_s = \bar{a}_s.$$

(2) Proof for $\sigma(\hat{\theta}_s^w) = \sigma(\bar{a}_s)$

From proposition (P5.2) concerning the error of the inverse adjustment factor we have that $\tau_s = \gamma_s q_s^{-1} \sigma(q_s)$. From equation (E5.7), ignoring the approximation, we also have that

$$\begin{aligned}\sigma^2(\hat{\theta}_s^w) &= \gamma_s^2 (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1})^{-1} + \gamma_s^4 \tau_s^2 (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1})^{-4} (\mathbf{1}^T \lambda_s)^2 \\ \lambda_s &= (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1}) \Sigma_{\phi_s}^{-1} \phi_s - 2 (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \phi_s) \Sigma_{\phi_s}^{-1} \mathbf{1}\end{aligned}$$

$$\begin{aligned}\text{Now } \mathbf{1}^T \lambda_s &= (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1})^{-1} (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \phi_s) - 2 (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1})^{-1} (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \phi_s) \\ &= - (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1})^{-1} (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \phi_s) \\ &= - \gamma_s^3 v_s u_s \\ &= - \gamma_s^3 v_s^2 \bar{a}_s. \quad \text{see proof (1)}\end{aligned}$$

$$\begin{aligned}\text{Thus } \sigma^2(\hat{\theta}_s^w) &= \gamma_s^2 (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1})^{-1} + \gamma_s^4 \tau_s^2 (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1})^{-4} (\mathbf{1}^T \lambda_s)^2 \\ &= v_s^{-1} + \gamma_s^{-4} \tau_s^2 v_s^{-4} [- \gamma_s^3 v_s^2 \bar{a}_s]^2 \\ &= v_s^{-1} + \gamma_s^2 \tau_s^2 \bar{a}_s^2.\end{aligned}$$

$$\begin{aligned}\text{And } \sigma^2(\bar{a}_s) &= n_s^{-2} w_s^{-2} f_s^2 \mathbf{Var}(q_s s^*) \\ &= n_s^{-2} w_s^{-2} f_s^2 [q_s^2 \mathbf{Var}(s^*) + [s^*]^2 \sigma^2(q_s)] \\ &= n_s^{-2} \gamma_s^2 [n_s \sigma_s^2 + n_s^2 \sigma_b^2] + n_s^{-2} [\gamma_s q_s^{-1} \sigma(q_s)]^2 [s^*]^2 \\ &= \gamma_s^2 [n_s^{-1} \sigma_s^2 + \sigma_b^2] + n_s^{-2} \tau_s^2 [n_s \gamma_s \bar{a}_s]^2 \\ &= v_s^{-1} + \gamma_s^2 \tau_s^2 \bar{a}_s^2. \quad \text{from proof (1)} \\ &= \sigma^2(\hat{\theta}_s^w)\end{aligned}$$

Proof (P5.8) for the Error of the Age of a Sample

- *proof for:*

$$\left. \begin{aligned} \sigma(\hat{t}^w) &\simeq 8033 \times \left[[\hat{\theta}_{\text{ox}}^w]^{-2} \sigma^2(\hat{\theta}_{\text{ox}}^w) + [\hat{\theta}_s^w]^{-2} \sigma^2(\hat{\theta}_s^w) \right. \\ &\quad \left. \dots - 2 [\hat{\theta}_{\text{ox}}^w]^{-1} [\hat{\theta}_s^w]^{-1} \text{Cov}(\hat{\theta}_{\text{ox}}^w, \hat{\theta}_s^w) \right]^{\frac{1}{2}} \\ \text{Cov}(\hat{\theta}_{\text{ox}}^w, \hat{\theta}_s^w) &= \sigma_b^2 \gamma_s (\pi^T \Sigma_\phi^{-1} \pi)^{-1} (\pi^T \Sigma_\phi^{-1} \mathbf{1}) \end{aligned} \right\}$$

Let us define the vector

$$\alpha = \begin{pmatrix} \hat{\theta}_{\text{ox}}^* \\ \hat{\theta}_s^w \end{pmatrix}, \quad \hat{\theta}_{\text{ox}}^* = 0.95 \hat{\theta}_{\text{ox}}^w$$

The covariance matrix for this vector is

$$\Sigma_\alpha = \begin{pmatrix} \sigma^2(\hat{\theta}_{\text{ox}}^*) & \text{Cov}(\hat{\theta}_{\text{ox}}^*, \hat{\theta}_s^w) \\ \text{Cov}(\hat{\theta}_{\text{ox}}^*, \hat{\theta}_s^w) & \sigma^2(\hat{\theta}_s^w) \end{pmatrix}$$

Now the function that we are interested in is

$$f(\alpha) = \log_e [\hat{\theta}_s^w]^{-1} \hat{\theta}_{\text{ox}}^*$$

and the vector of derivatives pertaining to this function is

$$\begin{aligned}
\mathbf{d}f &= \begin{pmatrix} \frac{df}{d\hat{\theta}_{\text{ox}}^*} \\ \frac{df}{d\hat{\theta}_s^w} \end{pmatrix} \\
&= \begin{pmatrix} [\hat{\theta}_{\text{ox}}^*]^{-1} \\ [-\hat{\theta}_s^w]^{-1} \end{pmatrix}
\end{aligned}$$

Since $\hat{t} = 8033 f(\alpha)$ we finally have that

$$\begin{aligned}
\sigma(\hat{t}) &\simeq 8033 [\mathbf{d}f^T \Sigma_\alpha \mathbf{d}f]^{\frac{1}{2}} \\
&= 8033 [[\hat{\theta}_{\text{ox}}^*]^{-2} \sigma^2(\hat{\theta}_{\text{ox}}^*) + [\hat{\theta}_s^w]^{-2} \sigma^2(\hat{\theta}_s^w) \\
&\quad \dots - 2 [\hat{\theta}_{\text{ox}}^*]^{-1} [\hat{\theta}_s^w]^{-1} \mathbf{Cov}(\hat{\theta}_{\text{ox}}^*, \hat{\theta}_s^w)]^{\frac{1}{2}} \\
&= 8033 [[\hat{\theta}_{\text{ox}}^w]^{-2} \sigma^2(\hat{\theta}_{\text{ox}}^w) + [\hat{\theta}_s^w]^{-2} \sigma^2(\hat{\theta}_s^w) \\
&\quad \dots - 2 [\hat{\theta}_{\text{ox}}^w]^{-1} [\hat{\theta}_s^w]^{-1} \mathbf{Cov}(\hat{\theta}_{\text{ox}}^w, \hat{\theta}_s^w)]^{\frac{1}{2}}
\end{aligned}$$

The form of the covariance term is

$$\begin{aligned}
\mathbf{Cov}(\hat{\theta}_{\text{ox}}^w, \hat{\theta}_s^w) &= \gamma_s (\pi^T \Sigma_\phi^{-1} \pi)^{-1} (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1})^{-1} \pi^T \Sigma_\phi^{-1} \mathbf{Cov}(\phi, \phi_s) \Sigma_{\phi_s}^{-1} \mathbf{1} \\
&= \sigma_b^2 \gamma_s (\pi^T \Sigma_\phi^{-1} \pi)^{-1} (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1})^{-1} (\pi^T \Sigma_\phi^{-1} \mathbf{1}) (\mathbf{1}^T \Sigma_{\phi_s}^{-1} \mathbf{1}) \\
&= \sigma_b^2 \gamma_s (\pi^T \Sigma_\phi^{-1} \pi)^{-1} (\pi^T \Sigma_\phi^{-1} \mathbf{1})
\end{aligned}$$

This completes the proof.

6 Comparison of Age Estimators

In order to compare the relative merits of the conventional and weighted least squares estimators it is of interest to set up a simulation study which will put these two methods to the test. The basic idea is to get a reasonable picture of a 'typical' batch of samples and then reproduce some new samples on the basis of this information.

Two features of the estimators will be considered, namely bias and error. It is hoped that both estimators will demonstrate negligible bias on average. It is expected that this will be the case since both estimators are theoretically unbiased estimators. It is also therefore expected that neither will have any great advantage over the other in this respect. The consideration of error, however, may prove to be a different case. It is expected that the error for the weighted least squares estimator will prove to be superior. This expectation is founded on the results presented in the previous section as well as on the fact that the weighted least squares estimator is uniformly minimum variance unbiased according to the model proposed for the data.

The simulation is conducted in three stages. The first stage is to take a typical pool of samples and determine the relevant components of variation; in this case, within-batch, across-batch and across-sample variation. The second stage is to reconstruct samples of known radiocarbon age from the information stemming from the first stage. Once these samples are generated, the last stage is to apply the age estimators to the synthetic data and assess their respective merits.

6.1 Stage 1: Building a Picture of Samples

The data used to construct a picture of samples spans the period of time from 3/4/84 till 24/7/84 (used in the data application in section 5.6.9). This period of time is ideal since it is known to constitute a period of relative stability. From the chemist's point of view 'stability' means satisfactory performance of samples and equipment.

The data are sorted into two groups. The first group constitutes all background samples over this time interval and the second group all standard samples. These two groups are examined separately and a general picture of background and standard sample behaviour is drawn from them. A similar study for field samples is unnecessary since it is possible to generate such samples from a knowledge of the oxalic standard activity and the mathematical relationship between the age of a sample and its own activity (see section 6.2.3). An important point in favour of this data is that the same four background samples and the same four standard samples appear over the eight relevant batches.

There are four components of sample activity which are evaluated in order to determine typical sample behaviour. These components are the overall average sample activity, the variation across samples, the variation across batches and the variation across cycles (within-batch). These are all required to generate new data. It is simpler to investigate the background samples first.

6.1.1 A Picture of Background Samples

Background samples are easier to deal with since their activities are not confounded with other kinds of activities. It is therefore a relatively simple matter to evaluate the four

components of sample behaviour, that is, the grand mean activity (derived over all samples, batches and cycles) and the three relevant components of variation. A suitable model is proposed to allow these four components to be evaluated. This model is

$$B_{ijk} = \mu_b + A_i + B_j + C_{k(ij)}, \quad \left. \begin{array}{l} i = 1, \dots, I, \\ j = 1, \dots, J, \\ k = 1, \dots, K_{ij} \end{array} \right\}$$

where $A_i \sim N(0, \sigma_A^2)$

$$B_j \sim N(0, \sigma_B^2)$$

$$C_{k(ij)} \sim N(0, \sigma_C^2)$$

The term B_{ijk} denotes the observation for the i th background sample in the j th batch at the k th cycle. The term μ_b denotes the true mean background activity over the relevant period of time. The estimate of this parameter is not of great significance since it is clearly dependent on the chosen period of time.

The first component of variation A_i represents the contribution to total variation incurred by the i th sample. The second component of variation B_j represents the contribution to total variation incurred by the j th batch. The batch effect is taken to be independent of the sample effect because shifts in the background activity over time are presumed to uniformly affect all background samples. This is to conform to the results in section 4.1.1 which show that differences between samples across time may be considered to be constant. The final component of variation $C_{(ij)k}$ is a nested term and represents the within-batch variation.

This model is unbalanced — the number of cycles is not the same for each sample in each batch. To derive estimates for the four components of interest, the following four statistics are employed:

$$B_0 = [\sum_{i=1}^I \sum_{j=1}^J K_{ij}]^{-1} \sum_{i=1}^I \sum_{j=1}^J \sum_{k=1}^{K_{ij}} B_{ijk}$$

$$B_1 = \frac{1}{IJ} \sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}-1} \sum_{k=1}^{K_{ij}} (B_{ijk} - \bar{B}_{ij.})^2$$

$$B_2 = \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J (\bar{B}_{ij.} - \bar{B}_{i..})^2$$

$$B_3 = \frac{1}{(I-1)} \sum_{i=1}^I (\bar{B}_{i..} - \bar{B}_{...})^2$$

where $\bar{B}_{ij.} = \frac{1}{K_{ij}} \sum_{k=1}^{K_{ij}} B_{ijk}$

$$\bar{B}_{i..} = \frac{1}{J} \sum_{j=1}^J \bar{B}_{ij.}$$

$$\bar{B}_{...} = \frac{1}{I} \sum_{i=1}^I \bar{B}_{i..}$$

The statistics B_1 , B_2 , and B_3 are just standard sums of squares employed in the analysis of variance. Using these statistics it is relatively easy to derive the following unbiased estimators:

$$\left. \begin{aligned} \hat{\mu}_B &= B_0 \\ \hat{\sigma}_C^2 &= B_1 \\ \hat{\sigma}_B^2 &= B_2 - \frac{1}{IJ} [\sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}}] \hat{\sigma}_C^2 \\ \hat{\sigma}_A^2 &= B_3 - \frac{1}{J} \hat{\sigma}_B^2 - \frac{1}{IJ^2} [\sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}}] \hat{\sigma}_C^2 \end{aligned} \right\} \quad (E6.1)$$

Justification for these results is given in proof (P6.1) at the end of this section. Applying equations (E6.1) to the data gives us the following results:

$$\hat{\mu}_B = 7.7607$$

$$\hat{\sigma}_C^2 = 0.2134$$

$$\hat{\sigma}_B^2 = 0.0508$$

$$\hat{\sigma}_A^2 = 0.0000$$

The sample variance was slightly negative but is rounded to zero in order to make the results sensible. It can be seen from the above results that the cycles are clearly the largest source of variation with samples contributing the least. This is good because it suggests a relative uniformity of the samples and a relative stability across the batches.

From this information it is possible to reconstruct new background samples although it is understood that this information reflects a particular period of time. There is no reason, however, to believe that this is a peculiar period of time and the results here are considered to be of a general nature. (The grand mean is obviously closely related to the time interval but the evaluated components of variation are assumed to be general results.)

6.1.2 A Picture of Standard Samples

A complication in the study of standard samples is that standard sample activities are confounded with the background activity. This needs to be taken into account when proposing a suitable model for the standard sample data. In addition, it is necessary to take into account the relationship between gross counts and normalised activities.

With all of these factors taken into account, the appropriate model for the standard sample data is

$$M_{ijk} = c_{ij}(\lambda_m + D_i + E_j + F_{k(ij)}) + \mu_b + A_i + B_j + C_{k(ij)}, \quad \left. \begin{array}{l} i = 1, \dots, I, \\ j = 1, \dots, J, \\ k = 1, \dots, K \end{array} \right\}$$

where $c_{ij} = w_i \cdot f_i^{-1} \cdot q_{ij}^{-1}$ (the inverse adjustment factor)

$$D_i \sim N(0, \sigma_D^2)$$

$$E_j \sim N(0, \sigma_E^2)$$

$$F_{k(ij)} \sim N(0, \sigma_F^2)$$

This time the data are balanced. This makes the task marginally easier although the complexity of the model itself means that it is not entirely a straightforward matter to derive estimates for the four components of interest, namely $\{\lambda_m, \sigma_D, \sigma_E, \sigma_F\}$. The four terms $\{\mu_b, A_i, B_j, C_{k(ij)}\}$ in the above model are to be understood as being the same terms incorporated in the model for the background sample data. Thus independent estimates already exist for each of the components associated with these terms. This must be the case since without these independent estimates there is no way of separating out the terms sharing the same subscript in the above model.

In a roughly similar fashion to the study of the background samples, the following four statistics are employed:

$$\begin{aligned}
M_0 &= \frac{1}{K} [\sum_{i=1}^I \sum_{j=1}^J c_{ij}^2]^{-1} \sum_{i=1}^I \sum_{j=1}^J \sum_{k=1}^K c_{ij} M_{ijk} \\
M_1 &= \frac{1}{IJ(K-1)} \sum_{i=1}^I \sum_{j=1}^J \sum_{k=1}^K (M_{ijk} - \bar{M}_{ij.})^2 \\
M_2 &= \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J (\bar{M}_{ij.} - \bar{M}_{i..})^2 \\
M_3 &= \frac{1}{(I-1)} \sum_{i=1}^I (\bar{M}_{i..} - \bar{M}_{...})^2
\end{aligned}$$

where

$$\begin{aligned}
\bar{M}_{ij.} &= \frac{1}{K} \sum_{k=1}^K M_{ijk} \\
\bar{M}_{i..} &= \frac{1}{J} \sum_{j=1}^J \bar{M}_{ij.} \\
\bar{M}_{...} &= \frac{1}{I} \sum_{i=1}^I \bar{M}_{i..}
\end{aligned}$$

Using these statistics it is possible to derive the following unbiased pair of estimators for two of the parameters of interest:

$$\left. \begin{aligned}
\hat{\lambda}_m &= M_0 - [\sum_{i=1}^I \sum_{j=1}^J c_{ij}^2]^{-1} [\sum_{i=1}^I \sum_{j=1}^J c_{ij}] \hat{\mu}_b \\
\hat{\sigma}_F^2 &= [\frac{1}{IJ} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2]^{-1} (M_1 - \hat{\sigma}_C^2)
\end{aligned} \right\} \quad (E6.2)$$

The other two components of variance are derived from the following simultaneous equations:

$$\left. \begin{aligned}
k_2 \hat{\sigma}_D^2 + k_1 \hat{\sigma}_E^2 &= M_2 - k_2 \hat{\lambda}_m^2 - \frac{1}{K} k_1 \hat{\sigma}_F^2 - \hat{\sigma}_B^2 - \frac{1}{K} \hat{\sigma}_C^2 \\
k_4 \hat{\sigma}_D^2 + \frac{1}{K} k_1 \hat{\sigma}_E^2 &= M_3 - k_3 \hat{\lambda}_m^2 - \frac{1}{JK} k_1 \hat{\sigma}_F^2 \\
\dots &- \hat{\sigma}_A^2 - \frac{1}{J} \hat{\sigma}_B^2 - \frac{1}{JK} \hat{\sigma}_C^2
\end{aligned} \right\} \quad (E6.3)$$

$$\begin{aligned}
\text{where} \quad k_1 &= \frac{1}{IJ} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2 \\
k_2 &= \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J (c_{ij} - \bar{c}_{i.})^2 \\
k_3 &= \frac{1}{(I-1)} \sum_{i=1}^I (\bar{c}_{i.} - \bar{c}_{..})^2 \\
k_4 &= \frac{1}{I} \sum_{i=1}^I \bar{c}_{i.}^2 \\
\bar{c}_{i.} &= \frac{1}{J} \sum_{j=1}^J c_{ij} \\
\bar{c}_{..} &= \frac{1}{I} \sum_{i=1}^I \bar{c}_{i.}
\end{aligned}$$

The proofs for (E6.2) and (E6.3) are given in proof (P6.2) at the end of this section. These equations yield the following results from the data:

$$\begin{aligned}
\hat{\lambda}_m &= 9.3890 \\
\hat{\sigma}_F^2 &= 0.0453 \\
\hat{\sigma}_E^2 &= 0.0052 \\
\hat{\sigma}_D^2 &= 0.0000
\end{aligned}$$

This completes the picture for standard samples. It is similar in certain respects to the picture for background samples. The cycle variance is greater than the batch variance and this in turn is greater than the sample variance. (The sample variance is also rounded to zero as before.) This again is an encouraging result from the chemist's consideration since it demonstrates a relative stability of samples and batches.

6.2 Stage 2: Generating New Data

New samples are now generated from the information obtained in the previous stage of the study. The information acquired is adequate for the reproduction of new background,

standard and field sample data. Each of these types of samples is generated in turn.

6.2.1 Generating Background Samples

Generation of background samples involves three basic steps :-

1. Adding the Sample Component

Although the sample variance proved to be zero, it is useful to set this component to a very small value, say 0.0010. This ensures that different samples are generated with slightly different baseline values. Four values are initially produced to comply with the standard laboratory practice of employing four background samples in any batch. These four sample values are generated according to the equations

$$X_i = 7.7607 + \epsilon_i, \quad i = 1, \dots, 4$$
$$\epsilon_i \sim N(0, 0.0010)$$

2. Adding the Batch Component

Six batches are now reproduced for each of the four sample values to generate a total of 24 batch-sample values. The choice of six batches is based on the standard laboratory practice of estimating the age of a sample over six (or thereabouts) batches. To reproduce a single batch, an identical $N(0, 0.0508)$ gaussian variate is added to each of the four sample values. This is performed six times in order to reproduce the six required batches. The equations for this step are

$$X_{ij} = X_i + \epsilon_j, \quad i = 1, \dots, 4, j = 1, \dots, 6$$

$$\epsilon_j \sim N(0, 0.0508)$$

3. Adding the Cycle Component

The last step is to add the final component of variation to the batch-sample values in order to recreate the cycles of the dating procedure. To do this, ten individual $N(0, 0.2134)$ variates are added to each of the 24 batch-sample values to produce a total of 240 generated background data. The choice of ten is again standard. The equations for this final step are

$$X_{ijk} = X_{ij} + \epsilon_{k(ij)}, \quad \left. \begin{array}{l} i = 1, \dots, 4, \\ j = 1, \dots, 6, \\ k = 1, \dots, 10 \end{array} \right\}$$

$$\epsilon_{k(ij)} \sim N(0, 0.2134)$$

These three steps should theoretically produce new background data which are similar in character to the original data. This is useful because it means that fresh data can be generated every time the age of a sample is to be determined.

6.2.2 Generating Standard Samples

This is similar to the above procedure for generating background samples except at the cycle component stage where adjustment factors and background activity need to be taken into account.

1. Adding the Sample Component

As before a small component of variance is used here.

$$Y_i = 9.3890 + \epsilon_i, \quad i = 1, \dots, 4$$

$$\epsilon_i \sim N(0, 0.0010)$$

2. Adding the Batch Component

$$Y_{ij} = Y_i + \epsilon_j, \quad i = 1, \dots, 4, j = 1, \dots, 6$$

$$\epsilon_j \sim N(0, 0.0052)$$

3. Adding the Cycle Component

In this final step the cycles are recreated and at the same time the values are transformed to gross counts per minute. This is to reflect a real data situation in which gross counts are observed and not the true sample activities. This combination of adding the cycle component and transforming the data is expressed in the equations

$$Y_{ijk} = c_{ij} \times (Y_{ij} + \epsilon_{k(ij)}) + X_{ijk}^*, \quad \left. \begin{array}{l} i = 1, \dots, 4, \\ j = 1, \dots, 6, \\ k = 1, \dots, 10 \end{array} \right\}$$

$$\epsilon_{k(ij)} \sim N(0, 0.0453)$$

The term X_{ijk}^* denotes a background observation thrown up by the background activity, this being generated as previously outlined for background data. Thus it is necessary to generate another four background samples in addition to the four already

generated. (The use of the asterisk is to distinguish this background data as separate from the background samples already generated.) The inverse adjustment factor c_{ij} is relatively unimportant here since adjustment factors are roughly equal in practice for standard samples and this factor will disappear, at any rate, when calculating the the normalised sample activity. Due to its relative unimportance, this factor will be taken to be unity for all samples over all batches. A token error is retained.

6.2.3 Generating Samples with Known Radiocarbon Ages

The data is incomplete without some field samples. These samples need to possess a known radiocarbon age in order to assess the merits of the two age estimators. The generation of these samples is made possible according to the formula that expresses the relationship between a sample's age, its true activity and the true standard activity. By making the true sample activity the subject of the equation we have that

$$\theta_s = 0.95 \theta_{ox} \exp(-\lambda^{-1} t) \quad (E6.4)$$

where θ_s = true sample activity
 θ_{ox} = true standard activity
 t = radiocarbon age of sample
 λ = known constant

To generate data for a sample of given age t , it is therefore necessary to generate another standard sample independently of the four samples already generated. This standard sample will itself require another background sample to be generated. The sample is then produced according to equation (E6.4).

This completes the data generation for one group of data: a group of data spans six batches each containing four background samples, four standard samples and one field sample of known radiocarbon age. With this 'typical' data it is now possible to estimate the age of the relevant field sample using the two age estimators. This makes a comparison possible.

6.3 Stage 3: Comparison Study

The conventional and weighted least squares age estimators are now applied to some synthetic data. To do this half a million $N(0, 1)$ variates are generated and used to reproduce data according to the steps outlined in stage 2 of the experiment. A total of 20 ages are examined between 500 and 10000 radiocarbon years old. The ages are in steps of 500 years between these two extremes. Each age is assessed using 20 independent groups of data. (It is useful to remember that each group of data comprises 9 samples over 6 batches.)

It would be impractical to present all results for each application of each age estimator to the 400 sets of data. Instead, box-plots are constructed from the results for each age. The box-plots in Figure 12 are of the biases of the estimates of age plotted for each age. Three main conclusions are drawn from these plots. The first conclusion is that there is no significant difference between the two estimators in terms of bias. The differences are negligible and it can be clearly seen that pairs of box-plots for each age are virtually identical. The second conclusion, taking only the median estimates of age into consideration, is that both estimators do not appear to demonstrate significant bias. The median values appear to fluctuate closely around zero. The third and final conclusion that is drawn from the plots is that although the biases appear to be zero on average, larger discrepancies in individual instances of bias are observed as the age increases. This is to be expected

Figure 12: box-plots of bias for the two age estimators

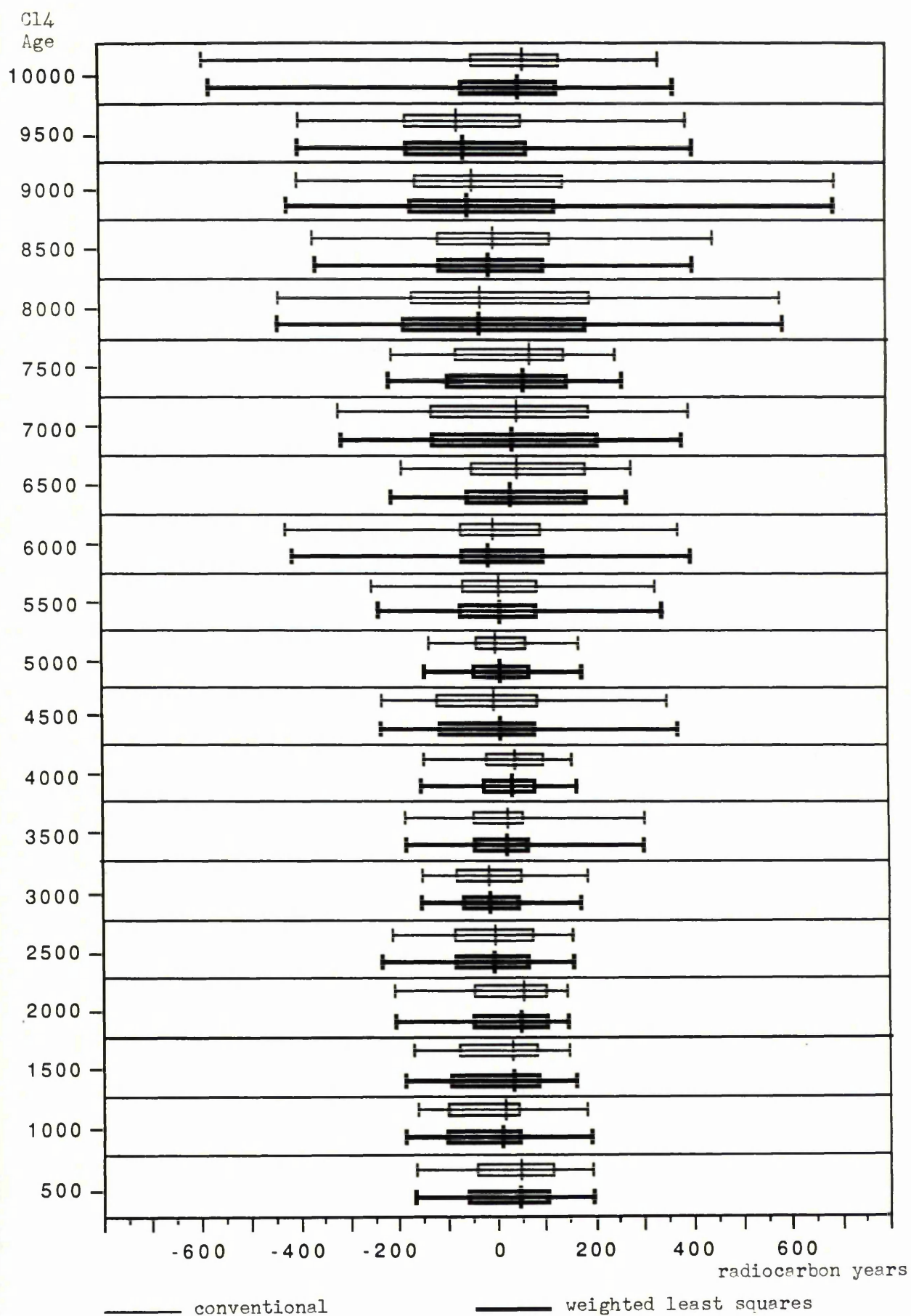
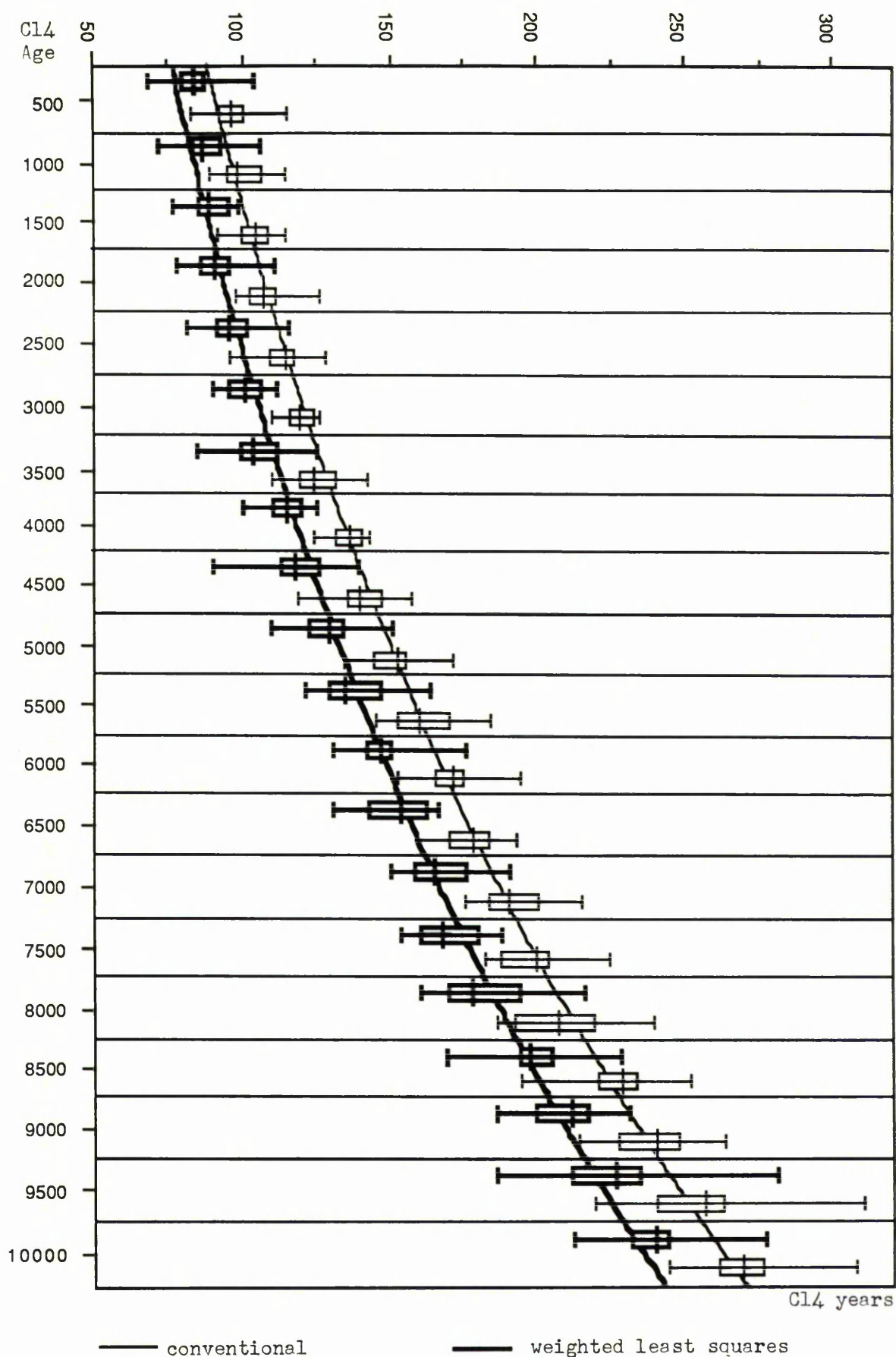


Figure 13: box-plots of errors for the two age estimators



since the error associated with older samples is greater. Discrepancies of around 200 to 300 radiocarbon years in either direction are observed for ages of 500 to 5500 radiocarbon years. Larger discrepancies of 300 to 700 radiocarbon years in either direction are observed for ages between 6000 and 10000 radiocarbon years.

None of the conclusions drawn above are really surprising. The first two conclusions about similarity and negligibility of bias are really just a consequence of the two estimators being unbiased estimators of age. Thus there is no particular advantage with respect to bias in using either estimator.

The picture of the errors, however, tells a different story. Box-plots for the errors are shown in Figure 13. Three conclusions are drawn from these plots. The first is that the errors corresponding to the weighted least squares estimates are consistently smaller than those of the conventional estimates. The pairs of box-plots for each age appear to be similar in size and shape but not in location. The box-plots for the weighted least squares estimates are shifted down from the box-plots for the conventional estimates and the shifts appear to follow a pattern determined by two exponential curves which constitute a reasonable fit to the median values of the errors corresponding to both estimators. (The difference between the errors is quantified shortly.) The second conclusion to be drawn is that the errors of both estimators increase exponentially as age increases. The rate of increase is notably greater for the conventional estimator. The last conclusion drawn from these plots is that the errors of older samples are generally wider in range, this fact demonstrated by the longer box-plots for older samples. This is due to the expected increase in the error of errors for older samples.

The overall conclusion that can be made about the two age estimators in the light of

the above results, is that the weighted least squares estimator has the advantage in terms of error, if not in terms of accuracy. The improvement in error for this estimator is due to the greater precision in the specification of error. This was seen in section 5 where it was shown that correlation among background corrected data should be taken into account. The specified error for the conventional estimator is only an approximation. An exact specification for the error of the conventional estimator is not given in this study but it may be of interest to make such a specification in a future study.

To quantify the difference between the two estimators, means for each estimator with respect to each age are presented in Table 12. The quoted means are the mean estimates of age and the mean errors, each of these being calculated from the 20 results produced for each estimator with respect to each age. (NB! The quoted errors should not be construed as the errors of the averages but rather the averages of the errors.)

The biases corresponding to both estimators are small and similar. The average absolute bias is 17.4 radiocarbon years for the weighted least squares estimator and 18.0 radiocarbon years for the conventional estimator. This does not constitute an appreciable difference. The error difference, however, is considerable. The average percentage difference is a relative 16.6% reduction in favour of the weighted least squares estimator. In section 5.6.9 the average percentage difference observed for a single batch was 8.5%. It is only to be expected that a greater error difference will be observed for a greater amount of data pooled over a number of batches.

In conclusion, the results of this comparison suggest that the weighted least squares estimator is a highly useful estimator and may be safely employed in place of the conventional estimator. Although it does not offer significantly greater accuracy, it does offer considerable

¹⁴ C Age (a)	<i>weighted least squares</i>		<i>conventional</i>		bias		% error difference
	estimate (b)	error (c)	estimate (d)	error (e)	(b)-(a)	(d)-(a)	[(e)-(c)]/(e)×100%
500	525	85	530	97	+25	+30	14.12
1000	990	88	991	101	-10	-9	14.77
1500	1499	89	1502	104	-1	+2	16.85
2000	2022	92	2024	109	+22	+24	18.48
2500	2490	97	2497	115	-10	-3	18.56
3000	2993	101	2992	120	-7	-8	18.81
3500	3514	105	3511	126	+14	+11	20.00
4000	4028	114	4030	137	+28	+30	20.18
4500	4497	119	4495	141	-3	-5	18.49
5000	5019	128	5014	151	+19	+14	17.97
5500	5509	138	5508	163	+9	+8	18.12
6000	5999	147	5993	171	-1	-7	16.33
6500	6553	152	6557	178	+53	+57	17.11
7000	7039	167	7039	193	+39	+39	15.57
7500	7536	171	7535	199	+36	+35	16.37
8000	8007	182	8006	209	+7	+6	14.84
8500	8502	199	8500	227	+2	0	14.07
9000	8996	209	9004	239	-4	+4	14.35
9500	9462	226	9457	256	-38	-43	13.27
10000	10019	239	10024	270	+19	+24	12.97

Table 12: mean results for estimates of age and errors of estimates of age

improvement in precision and size of error. Caution must be exercised, however, since the issue of error multiplication would need to be carefully considered before employing the weighted least squares method. A laboratory which is already significantly underestimating its own internal variability would simply end up worsening its situation by adoption of the method without seeking to properly reflect true laboratory variability in its results.

6.4 Various Proofs

Proof (P6.1) for Error Terms (E6.3)

- *proof for:*

$$\hat{\sigma}_C^2 = B_1$$

By referring to model (E6.1) and the various associated sums of squares, the proof is as follows:

$$\begin{aligned} \mathbf{E}[(B_{ijk} - \bar{B}_{ij.})^2] &= \mathbf{E}[(C_{k(ij)} - \frac{1}{K_{ij}} \sum_{k=1}^{K_{ij}} C_{k(ij)})^2] \\ &= \sigma_C^2 - \frac{2}{K_{ij}} \sigma_C^2 + \frac{1}{K_{ij}} \sigma_C^2 \\ &= \frac{(K_{ij}-1)}{K_{ij}} \sigma_C^2 \end{aligned}$$

$$\begin{aligned} \text{i.e.} \quad \mathbf{E} B_1 &= \frac{1}{IJ} \sum_{i=1}^I \sum_{j=1}^J \frac{1}{(K_{ij}-1)} \sum_{k=1}^{K_{ij}} \frac{(K_{ij}-1)}{K_{ij}} \sigma_C^2 \\ &= \sigma_C^2 \end{aligned}$$

$$\text{Thus} \quad \hat{\sigma}_C^2 = B_1$$

- *proof for:*

$$\hat{\sigma}_B^2 = B_2 - \frac{1}{IJ} [\sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}}] \hat{\sigma}_C^2$$

The proof is :-

$$\begin{aligned} \mathbf{E}[(\bar{B}_{ij.} - \bar{B}_{i..})^2] &= \mathbf{E}[(B_j - \tfrac{1}{J} \sum_{j=1}^J B_j)^2] \\ &\dots + \mathbf{E}[(\tfrac{1}{K_{ij}} \sum_{k=1}^{K_{ij}} C_{k(ij)} - \tfrac{1}{J} \sum_{j=1}^J \tfrac{1}{K_{ij}} \sum_{k=1}^{K_{ij}} C_{k(ij)})^2] \end{aligned}$$

$$\begin{aligned}
&= \sigma_B^2 - \frac{2}{J} \sigma_B^2 + \frac{1}{J} \sigma_B^2 + \frac{1}{K_{ij}} \sigma_C^2 - \frac{2}{JK_{ij}} \sigma_C^2 + \frac{1}{J^2} \sum_{j=1}^J \frac{1}{K_{ij}} \sigma_C^2 \\
&= \frac{(J-1)}{J} \sigma_B^2 + \frac{(J-2)}{JK_{ij}} \sigma_C^2 + \frac{1}{J^2} \sum_{j=1}^J \frac{1}{K_{ij}} \sigma_C^2
\end{aligned}$$

$$\begin{aligned}
\text{i.e. } E B_2 &= \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J \left[\frac{(J-1)}{J} \sigma_B^2 + \frac{(J-2)}{JK_{ij}} \sigma_C^2 + \frac{1}{J^2} \sum_{j=1}^J \frac{1}{K_{ij}} \sigma_C^2 \right] \\
&= \sigma_B^2 + \left[\frac{(J-2)}{IJ(J-1)} \sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}} + \frac{1}{IJ(J-1)} \sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}} \right] \sigma_C^2 \\
&= \sigma_B^2 + \left[\frac{1}{IJ} \sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}} \right] \sigma_C^2
\end{aligned}$$

$$\text{So } \hat{\sigma}_B^2 = B_2 - \frac{1}{IJ} \left[\sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}} \right] \hat{\sigma}_C^2$$

• *proof for:*

$$\hat{\sigma}_A^2 = B_3 - \frac{1}{J} \hat{\sigma}_B^2 - \frac{1}{IJ^2} \left[\sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}} \right] \hat{\sigma}_C^2$$

The proof is :-

$$\begin{aligned}
E[(\bar{B}_{i..} - \bar{B}_{...})^2] &= E[(A_i - \frac{1}{I} \sum_{i=1}^I A_i)^2] \\
&\dots + E\left[\left(\frac{1}{J} \sum_{j=1}^J B_j - \frac{1}{IJ} \sum_{i=1}^I \sum_{j=1}^J B_j\right)^2\right] \\
&\dots + E\left[\left(\frac{1}{J} \sum_{j=1}^J \frac{1}{K_{ij}} \sum_{k=1}^{K_{ij}} C_{k(ij)} \right.\right. \\
&\quad \left.\left. - \frac{1}{IJ} \sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}} \sum_{k=1}^{K_{ij}} C_{k(ij)}\right)^2\right] \\
&= \sigma_A^2 - \frac{2}{I} \sigma_A^2 + \frac{1}{I} \sigma_A^2 + \frac{1}{J} \sigma_B^2 - \frac{2}{IJ} \sigma_B^2 + \frac{1}{IJ} \sigma_B^2 \\
&\dots + \frac{1}{J^2} \sum_{j=1}^J \frac{1}{K_{ij}} \sigma_C^2 - \frac{2}{IJ^2} \sum_{j=1}^J \frac{1}{K_{ij}} \sigma_C^2 \\
&\dots + \frac{1}{I^2 J^2} \sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}} \sigma_C^2
\end{aligned}$$

$$\begin{aligned}
&= \frac{(I-1)}{I} \sigma_A^2 + \frac{(I-1)}{IJ} \sigma_B^2 + \frac{(I-2)}{IJ^2} \sum_{j=1}^J \frac{1}{K_{ij}} \sigma_C^2 \\
&\dots + \frac{1}{I^2 J^2} \sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}} \sigma_C^2
\end{aligned}$$

$$\begin{aligned}
\text{i.e.} \quad \mathbf{E} B_3 &= \frac{1}{(I-1)} \sum_{i=1}^I \left[\frac{(I-1)}{I} \sigma_A^2 + \frac{(I-1)}{IJ} \sigma_B^2 + \frac{(I-2)}{IJ^2} \sum_{j=1}^J \frac{1}{K_{ij}} \sigma_C^2 \right. \\
&\quad \left. \dots + \frac{1}{I^2 J^2} \sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}} \sigma_C^2 \right] \\
&= \sigma_A^2 + \frac{1}{J} \sigma_B^2 + \left[\frac{(I-2)}{I(I-1)J^2} \sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}} \right. \\
&\quad \left. \dots + \frac{1}{I(I-1)J^2} \sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}} \right] \sigma_C^2 \\
&= \sigma_A^2 + \frac{1}{J} \sigma_B^2 + \left[\frac{1}{IJ^2} \sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}} \right] \sigma_C^2
\end{aligned}$$

$$\text{Thus} \quad \hat{\sigma}_A^2 = B_3 - \frac{1}{J} \hat{\sigma}_B^2 - \frac{1}{IJ^2} \left[\sum_{i=1}^I \sum_{j=1}^J \frac{1}{K_{ij}} \right] \hat{\sigma}_C^2$$

Proof (P6.2) for Mean and Error Terms (E6.3) & (E6.4)

• *proof for:*

$$\hat{\lambda}_m = M_0 - \left[\sum_{i=1}^I \sum_{j=1}^J c_{ij}^2 \right]^{-1} \left[\sum_{i=1}^I \sum_{j=1}^J c_{ij} \right] \hat{\mu}_b$$

By referring to model (E6.2) and the definition of M_0 , the proof is :-

$$\begin{aligned}
S(\lambda_m, \mu_b) &= \sum_{i=1}^I \sum_{j=1}^J \sum_{k=1}^K (M_{ijk} - \mathbf{E} M_{ijk})^2 \\
&= \sum_{i=1}^I \sum_{j=1}^J \sum_{k=1}^K (M_{ijk} - c_{ij} \lambda_m - \mu_b)^2
\end{aligned}$$

$$\frac{dS(\lambda_m, \mu_b)}{d\lambda_m} = -2 \sum_{i=1}^I \sum_{j=1}^J \sum_{k=1}^K c_{ij} (M_{ijk} - c_{ij} \lambda_m - \mu_b)$$

$$\frac{dS(\lambda_m, \mu_b)}{d\lambda_m} = 0 \quad \Rightarrow \quad \sum_{i=1}^I \sum_{j=1}^J \sum_{k=1}^K c_{ij} (M_{ijk} - c_{ij} \lambda_m - \mu_b) = 0$$

$$\text{So} \quad \hat{\lambda}_m = [\sum_{i=1}^I \sum_{j=1}^J c_{ij}^2]^{-1} [\frac{1}{K} \sum_{i=1}^I \sum_{j=1}^J \sum_{k=1}^K c_{ij} (M_{ijk} - \hat{\mu}_b)]$$

$$\text{i.e.} \quad \hat{\lambda}_m = M_0 - [\sum_{i=1}^I \sum_{j=1}^J c_{ij}^2]^{-1} [\sum_{i=1}^I \sum_{j=1}^J c_{ij}] \hat{\mu}_b$$

• *proof for:*

$$\hat{\sigma}_F^2 = [\frac{1}{IJ} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2]^{-1} (M_1 - \hat{\sigma}_C^2)$$

The proof is :-

$$\begin{aligned} \mathbf{E}[(M_{ijk} - \bar{M}_{ij})^2] &= c_{ij}^2 \mathbf{E}[(F_{k(ij)} - \frac{1}{K} \sum_{k=1}^K F_{k(ij)})^2] \\ &\dots + \mathbf{E}[(C_{k(ij)} - \frac{1}{K} \sum_{k=1}^K C_{k(ij)})^2] \\ &= c_{ij}^2 (\sigma_F^2 - \frac{2}{K} \sigma_F^2 + \frac{1}{K} \sigma_F^2) + \sigma_C^2 - \frac{2}{K} \sigma_C^2 + \frac{1}{K} \sigma_C^2 \\ &= c_{ij}^2 \frac{(K-1)}{K} \sigma_F^2 + \frac{(K-1)}{K} \sigma_C^2 \end{aligned}$$

$$\begin{aligned} \text{i.e.} \quad \mathbf{E} M_1 &= \frac{1}{IJ(K-1)} \sum_{i=1}^I \sum_{j=1}^J \sum_{k=1}^K [c_{ij}^2 \frac{(K-1)}{K} \sigma_F^2 + \frac{(K-1)}{K} \sigma_C^2] \\ &= [\frac{1}{IJ} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2] \sigma_F^2 + \sigma_C^2 \end{aligned}$$

$$\text{Thus} \quad \hat{\sigma}_F^2 = [\frac{1}{IJ} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2]^{-1} (M_1 - \hat{\sigma}_C^2)$$

- *proof for:*

Estimates $\hat{\sigma}_D^2$ and $\hat{\sigma}_E^2$ are derivable from the simultaneous equations

$$\left. \begin{aligned} k_2 \hat{\sigma}_D^2 + k_1 \hat{\sigma}_E^2 &= M_2 - k_2 \hat{\lambda}_m^2 - \frac{1}{K} k_1 \hat{\sigma}_F^2 - \hat{\sigma}_B^2 - \frac{1}{K} \hat{\sigma}_c^2 \\ k_4 \hat{\sigma}_D^2 + \frac{1}{K} k_1 \hat{\sigma}_E^2 &= M_3 - k_3 \hat{\lambda}_m^2 - \frac{1}{JK} k_1 \hat{\sigma}_F^2 \\ &\dots - \hat{\sigma}_A^2 - \frac{1}{J} \hat{\sigma}_B^2 - \frac{1}{JK} \hat{\sigma}_c^2 \end{aligned} \right\}$$

The proof is in two parts :-

$$\begin{aligned} (1) \quad \mathbf{E}[(\bar{M}_{ij} - \bar{M}_{i..})^2] &= \mathbf{E}[(c_{ij} - \frac{1}{J} \sum_{j=1}^J c_{ij})^2 \lambda_m] \\ &\dots + \mathbf{E}[(c_{ij} - \frac{1}{J} \sum_{j=1}^J c_{ij})^2 D_i^2] \\ &\dots + \mathbf{E}[(c_{ij} E_j - \frac{1}{J} \sum_{j=1}^J c_{ij} E_j)^2] \\ &\dots + \mathbf{E}[(\frac{1}{K} c_{ij} \sum_{k=1}^K F_{k(ij)} \\ &\dots - \frac{1}{JK} \sum_{j=1}^J c_{ij} \sum_{k=1}^K F_{k(ij)})^2] \\ &\dots + \mathbf{E}[(B_j - \frac{1}{J} \sum_{j=1}^J B_j)^2] \\ &\dots + \mathbf{E}[(\frac{1}{K} \sum_{k=1}^K C_{k(ij)} - \frac{1}{JK} \sum_{j=1}^J \sum_{k=1}^K C_{k(ij)})^2] \\ &= S_1 + S_2 + S_3 + S_4 + S_5 + S_6 \quad \text{say.} \end{aligned}$$

Examining each of these terms in turn, we have the following:

$$\begin{aligned} (a) \quad \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J S_1 &= \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J (c_{ij} - \frac{1}{J} \sum_{j=1}^J c_{ij})^2 \lambda_m^2 \\ &= \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J (c_{ij} - \bar{c}_{i.})^2 \lambda_m^2 \\ &= k_2 \lambda_m^2 \end{aligned}$$

$$\begin{aligned}
 (b) \quad \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J S_2 &= \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J (c_{ij} - \bar{c}_{i.})^2 \sigma_D^2 \\
 &= k_2 \sigma_D^2
 \end{aligned}$$

$$\begin{aligned}
 (c) \quad \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J S_3 &= \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J [c_{ij}^2 \sigma_E^2 - \frac{2}{J} c_{ij}^2 \sigma_E^2 \\
 &\quad \dots + \frac{1}{J^2} \sum_{j=1}^J c_{ij}^2 \sigma_E^2] \\
 &= \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J [c_{ij}^2 \frac{(J-2)}{J} \\
 &\quad \dots + \frac{1}{J^2} \sum_{j=1}^J c_{ij}^2] \sigma_E^2 \\
 &= [\frac{(J-2)}{IJ(J-1)} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2 \\
 &\quad \dots + \frac{1}{IJ(J-1)} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2] \sigma_E^2 \\
 &= [\frac{1}{IJ} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2] \sigma_E^2 \\
 &= k_1 \sigma_E^2
 \end{aligned}$$

$$\begin{aligned}
 (d) \quad \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J S_4 &= \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J [\frac{1}{K} c_{ij}^2 \sigma_F^2 - \frac{2}{JK} c_{ij}^2 \sigma_F^2 \\
 &\quad \dots + \frac{1}{J^2 K} \sum_{j=1}^J c_{ij}^2 \sigma_F^2] \\
 &= \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J [\frac{(J-2)}{JK} c_{ij}^2 \\
 &\quad \dots + \frac{1}{J^2 K} \sum_{j=1}^J c_{ij}^2] \sigma_F^2 \\
 &= [\frac{1}{IJK} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2] \sigma_F^2 \\
 &= \frac{1}{K} k_1 \sigma_F^2
 \end{aligned}$$

$$\begin{aligned}
 (e) \quad \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J S_5 &= \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J [\sigma_B^2 - \frac{2}{J} \sigma_B^2 + \frac{1}{J} \sigma_B^2] \\
 &= \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J [\frac{(J-1)}{J}] \sigma_B^2 \\
 &= \sigma_B^2
 \end{aligned}$$

$$\begin{aligned}
 (f) \quad \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J S_6 &= \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J [\frac{1}{K} \sigma_C^2 - \frac{2}{JK} \sigma_C^2 + \frac{1}{K} \sigma_C^2] \\
 &= \frac{1}{I(J-1)} \sum_{i=1}^I \sum_{j=1}^J [\frac{(J-1)}{JK}] \sigma_C^2 \\
 &= \frac{1}{K} \sigma_C^2
 \end{aligned}$$

Putting all of the above results together, we have that

$$\begin{aligned}
 E M_2 &= k_2 \lambda_m^2 + k_2 \sigma_D^2 + k_1 \sigma_E^2 \\
 &\quad \dots + \frac{1}{K} k_1 \sigma_F^2 + \sigma_B^2 + \frac{1}{K} \sigma_C^2
 \end{aligned}$$

$$\text{Thus} \quad k_2 \hat{\sigma}_D^2 + k_1 \hat{\sigma}_E^2 = M_2 - k_2 \hat{\lambda}_m^2 - \frac{1}{K} k_1 \hat{\sigma}_F^2 - \hat{\sigma}_B^2 - \frac{1}{K} \hat{\sigma}_C^2$$

$$\begin{aligned}
(2) \quad \mathbb{E}[(\bar{M}_{i..} - \bar{M}_{...})^2] &= \mathbb{E}[(\frac{1}{J} \sum_{j=1}^J c_{ij} - \frac{1}{IJ} \sum_{i=1}^I \sum_{j=1}^J c_{ij})^2 \lambda_m] \\
&\dots + \mathbb{E}[(\frac{1}{J} \sum_{j=1}^J c_{ij} D_i - \frac{1}{IJ} \sum_{i=1}^I \sum_{j=1}^J c_{ij} D_i)^2] \\
&\dots + \mathbb{E}[(\frac{1}{J} \sum_{j=1}^J c_{ij} E_j - \frac{1}{IJ} \sum_{i=1}^I \sum_{j=1}^J c_{ij} E_j)^2] \\
&\dots + \mathbb{E}[(\frac{1}{JK} \sum_{j=1}^J \sum_{k=1}^K c_{ij} F_{k(ij)} \\
&\dots - \frac{1}{IJK} \sum_{i=1}^I \sum_{j=1}^J \sum_{k=1}^K c_{ij} F_{k(ij)})^2] \\
&\dots + \mathbb{E}[(A_i - \frac{1}{I} \sum_{i=1}^I A_i)^2] \\
&\dots + \mathbb{E}[(\frac{1}{J} \sum_{j=1}^J B_j)^2] \\
&\dots + \mathbb{E}[(\frac{1}{JK} \sum_{j=1}^J \sum_{k=1}^K C_{k(ij)} \\
&\dots - \frac{1}{IJK} \sum_{i=1}^I \sum_{j=1}^J \sum_{k=1}^K C_{k(ij)})^2] \\
&= T_1 + T_2 + T_3 + T_4 + T_5 + T_6 + T_7 \quad \text{say}
\end{aligned}$$

Examining each of these terms in turn, we have the following:

$$\begin{aligned}
(a) \quad \frac{1}{(I-1)} \sum_{i=1}^I T_1 &= [\frac{1}{(I-1)} \sum_{i=1}^I (\frac{1}{J} \sum_{j=1}^J c_{ij} - \frac{1}{IJ} \sum_{i=1}^I \sum_{j=1}^J c_{ij})^2] \lambda_m^2 \\
&= [\frac{1}{(I-1)} \sum_{i=1}^I (\bar{c}_{i.} - \bar{c}_{..})^2] \lambda_m^2 \\
&= k_3 \lambda_m^2
\end{aligned}$$

$$\begin{aligned}
(b) \quad \frac{1}{(I-1)} \sum_{i=1}^I T_2 &= \frac{1}{(I-1)} \sum_{i=1}^I \left[\frac{1}{J^2} (\sum_{j=1}^J c_{ij})^2 \sigma_D^2 - \frac{2}{IJ^2} (\sum_{j=1}^J c_{ij})^2 \sigma_D^2 \right. \\
&\quad \left. \dots + \frac{1}{I^2 J^2} \sum_{i=1}^I (\sum_{j=1}^J c_{ij})^2 \sigma_D^2 \right] \\
&= \frac{1}{(I-1)} \sum_{i=1}^I \left[\frac{(I-2)}{IJ^2} (\sum_{j=1}^J c_{ij})^2 \right. \\
&\quad \left. \dots + \frac{1}{I^2 J^2} \sum_{i=1}^I (\sum_{j=1}^J c_{ij})^2 \right] \sigma_D^2 \\
&= \frac{1}{(I-1)} \left[\frac{(I-1)}{IJ^2} \sum_{i=1}^I (\sum_{j=1}^J c_{ij})^2 \right] \sigma_D^2 \\
&= \left[\frac{1}{I} \sum_{i=1}^I \bar{c}_i^2 \right] \sigma_D^2 \\
&= k_4 \sigma_D^2
\end{aligned}$$

$$\begin{aligned}
(c) \quad \frac{1}{(I-1)} \sum_{i=1}^I T_3 &= \frac{1}{(I-1)} \sum_{i=1}^I \left[\frac{1}{J^2} \sum_{j=1}^J c_{ij}^2 \sigma_E^2 - \frac{1}{IJ^2} \sum_{j=1}^J c_{ij}^2 \sigma_E^2 \right. \\
&\quad \left. \dots + \frac{2}{I^2 J^2} \sum_{j=1}^J c_{ij}^2 \sigma_E^2 \right] \\
&= \frac{1}{(I-1)} \sum_{i=1}^I \left[\frac{(I-2)}{IJ^2} \sum_{j=1}^J c_{ij}^2 + \frac{1}{I^2 J^2} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2 \right] \sigma_E^2 \\
&= \frac{1}{(I-1)} \left[\frac{(I-1)}{IJ^2} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2 \right] \sigma_E^2 \\
&= \left[\frac{1}{IJ^2} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2 \right] \sigma_E^2 \\
&= \frac{1}{J} k_1 \sigma_E^2
\end{aligned}$$

$$\begin{aligned}
(d) \quad \frac{1}{(I-1)} \sum_{i=1}^I T_4 &= \frac{1}{(I-1)} \sum_{i=1}^I \left[\frac{1}{J^2 K} \sum_{j=1}^J c_{ij}^2 \sigma_F^2 - \frac{2}{IJ^2 K} \sum_{j=1}^J c_{ij}^2 \sigma_F^2 \right. \\
&\quad \left. \dots + \frac{1}{I^2 J^2 K} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2 \sigma_F^2 \right] \\
&= \frac{1}{(I-1)} \left[\frac{(I-2)}{IJ^2 K} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2 \right. \\
&\quad \left. \dots + \frac{1}{IJ^2 K} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2 \right] \sigma_F^2 \\
&= \left[\frac{1}{IJ^2 K} \sum_{i=1}^I \sum_{j=1}^J c_{ij}^2 \right] \sigma_F^2 \\
&= \frac{1}{JK} k_1 \sigma_F^2
\end{aligned}$$

$$(e) \quad \frac{1}{(I-1)} \sum_{i=1}^I T_5 = \sigma_A^2$$

$$(f) \quad \frac{1}{(I-1)} \sum_{i=1}^I T_6 = \frac{1}{J} \sigma_B^2$$

$$(g) \quad \frac{1}{(I-1)} \sum_{i=1}^I T_7 = \frac{1}{JK} \sigma_C^2$$

The last three results are not fully presented here but are easily verified. Putting all of these results together, we have the following:

$$\begin{aligned}
E M_3 &= k_3 \lambda_m^2 + k_4 \sigma_D^2 + \frac{1}{K} k_1 \sigma_E^2 + \frac{1}{JK} k_1 \sigma_F^2 \\
&\quad \dots + \sigma_A^2 + \frac{1}{J} \sigma_B^2 + \frac{1}{JK} \sigma_C^2
\end{aligned}$$

$$\begin{aligned}
\text{i.e. } k_4 \hat{\sigma}_D^2 + \frac{1}{K} k_1 \hat{\sigma}_E^2 &= M_3 - k_3 \hat{\lambda}_m^2 - \frac{1}{JK} k_1 \hat{\sigma}_F^2 \\
&\quad \dots - \hat{\sigma}_A^2 - \frac{1}{J} \hat{\sigma}_B^2 - \frac{1}{JK} \hat{\sigma}_C^2
\end{aligned}$$

This completes the result since the equations produced in (1) and (2) can be used to derive the appropriate terms.

7 Description of Software

The software package which has emerged from this work has undergone one major and recent revision since the original version which was completed in 1985. This revision was undertaken for two main reasons: Dr. Cook at the East Kilbride laboratory requested that some additional features be integrated into the existing software; the author also desired to make the programs more lucid by adding more comments to them and by modularising the programs in a better fashion to make them easier to modify and extend in the future. The revised software is described here.

Due to the memory limitations of the relatively primitive and fast-becoming-obsolete Apple II Europlus microcomputer systems employed, the software had to be divided into two separate programs. This is not too much of an inconvenience. Both programs are written in the Fortran 80 microcomputer language. With a few modifications they could easily be adapted to a mainframe environment using an appropriate variant of the Fortran language — Fortran variants are unlikely to be greatly dissimilar.

Even with the splitting of the software into two individual program units, each program is still constrained by memory limitations to only utilise a selected number of statistical algorithms applied to a limited number of samples and cycles. This problem will shortly be overcome by the transference of the software to a more powerful IBM computer system. Important details such as the maximum number of samples and cycles, details which are implicit in array sizes in both programs, could be changed through rewriting the programs but such changes could only be safely carried out by taking into account the limitations of the statistical algorithms employed in both programs. For example, some algorithms may need to be modified and/or extended to deal with larger data sets.

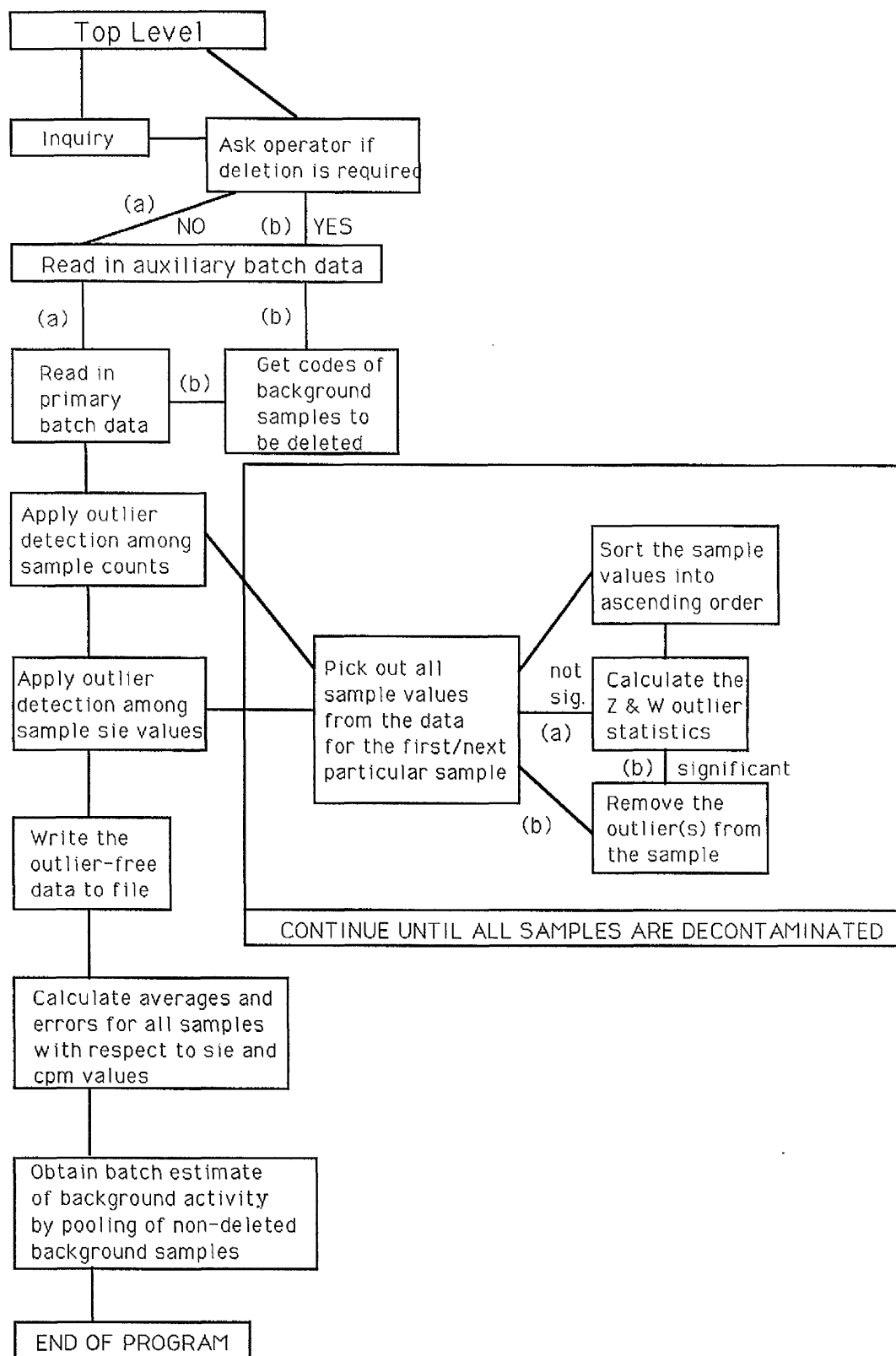
Descriptions of the two programs are each presented here in three parts: a brief program overview; an analysis of the program routines with descriptions of variables; a discussion of program limitations. The first program is referred to as the *outlier program* because one of its primary tasks is to screen the data for outliers and the second program is referred to as the *age program* because one of its primary tasks is to produce radiocarbon ages for all field samples. After both programs are described, the various input and output files which are connected with the programs are discussed including descriptions of data formats.

7.1 Description of the Outlier Program

The outlier program is fully presented in Appendix A of this report. Routines used by this program which are also used by the age program are presented in Appendix C which lists the shared routines. Figure 7.1 provides a sketch and abbreviation of the outlier program, demonstrating the nature and order of the tasks which it performs.

The program undertakes three main tasks once the data has been read in and any background samples which are required to be deleted from the calculation of the mean background activity have been communicated to the program. (Background samples would not be deleted unless they were seriously adrift relative to the main bulk of background samples and this would only be apparent after running the outlier program once, requiring the program to be run again if deletion is desired.) The first main task is the detection and elimination of contaminated data among sample cpm and sie values. The latter values are used in the evaluation of a quench correction factor (see description of the age program). The algorithm used to perform this task is based on the definitions of the Z and W statistics (E3.2) and on the linear equations (E3.3) which determine their critical values for a given

Figure 14 : illustration of outlier program



sample size n where n is not large (up to and including 12 observations). The second main task is to calculate averages for each sample with respect to both cpm and sie values. The third and final of the main tasks is to calculate a mean background activity and error by the pooling of all non-deleted background samples.

7.1.1 Analysis of Outlier Program Routines

The outlier program is comprised of 20 routines, 5 of which it shares with the age program. It is useful here to give explanations of each routine in the order in which they are called by the program. Comments already appear within the program itself. The explanations here place particular emphasis on descriptions of the main variables appearing throughout the program. Since variables appear in various routines, they are only listed in those routines in which they are first assigned values. The outlier program routines (those marked [†] appear in Appendix C) are :-

- (1) OUTLIE *Main Assigned Variable(s):* INTEGER KOUNT.

Top level routine which regulates the various tasks to be performed by the outlier program. The variable KOUNT signifies a task number which is included in the report generated by the program.

- (2) BLOCK1[†] See comment in program.

- (3) BLOCK2[†] See comment in program.

(4) OQUERY *Main Assigned Variable(s):* LOGICAL DELETE.

A question appears on the screen to be answered by the system operator:

DO YOU WANT THE OPTION TO DELETE? (Y/N):

The operator types Y or N depending on whether deletion of background samples from the calculation of the mean background activity is required or not. The variable DELETE is assigned the value of TRUE or FALSE accordingly. The actual execution of deletion does not occur until the auxiliary data has been read in (see next routine).

(5) INAXI[†] *Main Assigned Variable(s):* DIMENSION BATCH(30,4);
LOGICAL TYPE(30);
INTEGER NBATCH.

Auxiliary data is read in from the appropriate data file defining certain features of all samples belonging to the batch. The program presently caters for a maximum of 30 samples and 5 details concerning each sample are required to be communicated to the program: the sample number according to its position in the counting process; the sample type — a one character symbol indicating a background, modern standard, spiked or field sample; the sample code — a numerical label used by the laboratory for sample identification; the sample benzene weight in grams and the sample fractionation factor. The last two items are zero (any value will do!) for background samples since they are not relevant for that type of sample. Since the sample type is a non-numerical datum it is stored in the logical array TYPE. The other four items are stored in the

BATCH array in the order mentioned above and the number of samples read in is recorded in NBATCH.

(6) OPTION *Main Assigned Variable(s):* INTEGER BDLETE(6);
INTEGER NDLETE.

If the operator has requested deletion, then a question appears on the screen after the auxiliary data has been read in:

DO YOU WANT TO DELETE ANY BACKGROUND SAMPLE
FROM THE OVERALL ESTIMATE OF BACKGROUND? (Y/N):

The answer N results in the immediate exiting of the routine while the answer Y invokes the appearance on the screen of the prompt

TYPE IN BACKGROUND SAMPLE CODE (0 TO EXIT):

The operator responds by typing in the numerical code of a background sample which must match that of a background sample which has been read in from the auxiliary data file. Warning messages appear on the screen if an error is incurred. When a legitimate code is received it is stored in the BDLETE array. The option to delete keeps on looping until the operator types N in response to the question above. The total number of samples to be deleted is recorded in NDLETE.

(7) INDATA *Main Assigned Variable(s):* DIMENSION DATA(360,4);
INTEGER NDATA.

The main counting data is now read into the program one line at a time. Not

are multiplied by the corresponding values in TIME. The number of observations for the sample is recorded in NSAMPL.

- (10) SORT *Main Assigned Variable(s):* DIMENSION ARRAY1(12);
DIMENSION ARRAY2(12) .

Sample values are required to be sorted to allow the outlier detection statistics to be evaluated since they are functions of the order statistics. It may also be required to find the sample observation with the largest residual which can be done via sorting. The appropriate data to be sorted is placed into ARRAY1 and corresponding data (e.g. counting times) are placed into ARRAY2. The data in the first array are sorted into ascending order and the data in the second array are rearranged according to the permutation imposed on the data in the first array.

- (11) MEDIAN *Main Assigned Variable(s):* REAL RMED .

The median RMED is evaluated for an ordered set of sample values. The median is needed in the evaluation of the Z statistic and in the evaluation of residuals.

- (12) ZWSTAT *Main Assigned Variable(s):* REAL ZVAL;
REAL WVAL .

The outlier detection statistics ZVAL and WVAL are evaluated for the relevant set of sample values.

- (13) REPORT *Main Assigned Variable(s):* NONE .

Whenever a set of sample values is contaminated an appropriate message is

(14) RESIDU *Main Assigned Variable(s):* DIMENSION RESIJK(12).

$$r_i = \frac{|x_i - m_{-i}|}{G_{-i}^*}, \quad i = 1, \dots, n$$

```
(15)  CLEAN           Main Assigned Variable(s):  REAL XTREME;
                                           REAL UPPER;
                                           REAL LOWER.
```

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outlier-pair is removed and when the Z statistic is significant a single outlier is removed.

(16) NEWDAT *Main Assigned Variable(s):* NONE.

Once the data have been screened for outliers, the outlier-free data is written to an output data file which is used by the age program.

(17) AVRAGE Averages are evaluated for all samples.

(18) AVCALC *Main Assigned Variable(s):* AVSMPL(30,2).

Averages are produced for a sample with respect to both its sie and cpm values. As stated before, zero values are ignored. The average cpm and error are stored in AVSMPL in order to subsequently calculate the mean background activity.

(19) AVSTAN[†] *Main Assigned Variable(s):* REAL AV;
REAL SD.

An average (AV) and standard deviation (SD) are produced for an array of values.

(20) BACKGR *Main Assigned Variable(s):* REAL BACK;
REAL ERBK.

This final routine in the outlier program evaluates a mean background activity (BACK) and error (ERRBK). This is done by the pooling of all non-deleted background samples. A simple unweighted average of the samples is evaluated.

This completes the descriptions of the routines belonging to the outlier program. More detail than that which is supplied can only be obtained by a close examination of the actual

program itself but the above descriptions should help in the reading of the program.

7.1.2 Limitations of the Outlier Program

The outlier program has several limitations. It's generability is not as good as the age program which is discussed shortly. It also incorporates a number of laboratory idiosyncrasies which may not be pertinent to other laboratories. Some limitations/idiosyncrasies of the outlier program are :-

- (a) *Constraint on maximum size of samples.* This constraint is not one which can simply be removed by altering the appropriate array size — currently set at 12 — in the program. This could be done but it would need to be accompanied by modification of the outlier detection method which is only designed for small samples (see limitation of outlier detection method which follows). The maximum number of samples, however, is not constrained at all. The program presently caters for a maximum of 30 samples but this can be altered to any value within the bounds of common sense and computer memory.
- (b) *Outlier detection method inadequate for large samples.* The detection method was not designed for samples containing more than 12 observations. As such, it would be extremely unwise to apply the method to large samples since the linear regressions (E3.3) of the 99% quantiles of Z and W on the natural logarithms of the sample sizes may degenerate rapidly beyond 12 observations, either falling short of or rising away from the unseen points pertaining to larger samples. This would lead to underestima-

tion or overestimation, respectively, of the critical values of Z and W which indicate the likely presence of outliers in a sample. Even if the regressions are perfectly adequate for large samples, the detection statistics themselves are only designed to deal with two specific outlier situations, namely a single outlier and an upper and lower outlier-pair, which is wholly inadequate for large samples. To clarify on this point, it has not been uncommon to detect 1 outlier among samples of 10 observations on occasion and thus it would not be entirely infeasible that samples of a much larger size, say 60 observations, obtained through the aggregation of data from several batches, could generate 3 or more outliers in any one sample. The development of a broader detection method is therefore necessary if the data from batches are to be merged in the future at East Kilbride.

- (c) *Inclusion of sie values in data analyses.* This is a laboratory idiosyncrasy inasmuch as not all laboratories would include sie values in their data analyses. For example, some laboratories do not apply statistical quench corrections to their counting data while others do apply such corrections but do not use sie values as the means of applying them. If a different kind of data is used, then it may be possible to make changes in the programs which would accommodate alternative kinds of data. The outlier program, as it is presently written, searches for and eliminates outliers among the sie values and also reports averages for these values. This could be done for any kind of data.
- (d) *Calculation of mean background activity over-simplified.* The pooling of background samples in order to produce a mean background activity is not entirely satisfactory in its present form. First, there is no objective test for the presence of bias among

background samples. A straightforward one-way analysis of variance would suffice here and this is a feature that is being considered for future inclusion. Second, an unweighted average of the non-deleted background samples is far from optimal if any bias is truly present. A retrospect estimate of the background activity would alleviate this problem but is unfortunately not suitable here until three conditions are satisfied: a formula is specified for a retrospect estimator which accommodates more than one aligned sample; an acceptable definition is provided for 'alignment'; careful pooling of the data from the short 10 cycle batches into a single data set is carried out. This last condition is required since the pooling of the estimated ages of a field sample over six batches, say, would entail the pooling of six retrospect estimates — if such are used — of the background activity each drawing on an overlapping history of data, making the estimate of an error of age overly complicated. The retrospect estimate is designed to stand on its own as a single batch estimate and not to be combined. The proposed aggregation of the data from batches into a single large data set may facilitate adoption of retrospect estimation in the future.

- (e) *Inclusion of non-standard features.* There are a number of non-standard features in the outlier program which are worth mentioning here. The biggest of these features is a lower limit imposed on the error of the mean background activity. This is currently fixed at a value of 0.075 and is stored in the variable `BLIMIT` which is initialised in the block data subprogram `BLOCK2` and used in the subroutine `BACKGR`. This value is related to the maximum precision of background reproducibility of vials at the East Kilbride laboratory and is currently under review. A second non-standard feature is

the fixed nature of the protocol number in the program. This is clearly unfriendly to different data sets possessing different protocol numbers. A more flexible feature was not really required at East Kilbride but it might be useful to make it more flexible in the future. The third and final non-standard feature is the forcing of line feeding in writing to output files. This is a nuisance feature evident in the appearance of the variable LF throughout the program. This was a quirk of the Apple system and may not be applicable in a different system.

The above limitations and idiosyncrasies, particularly the limitation of the outlier detection method, reduce considerably the scope of the outlier program to effectively manage general types of counting data. It is broad enough to effectively manage one particular type of data but it needs to be broadened a lot more in order to make it flexible enough to manage other forms of data, particularly data corresponding to counting series which are longer than 12 cycles.

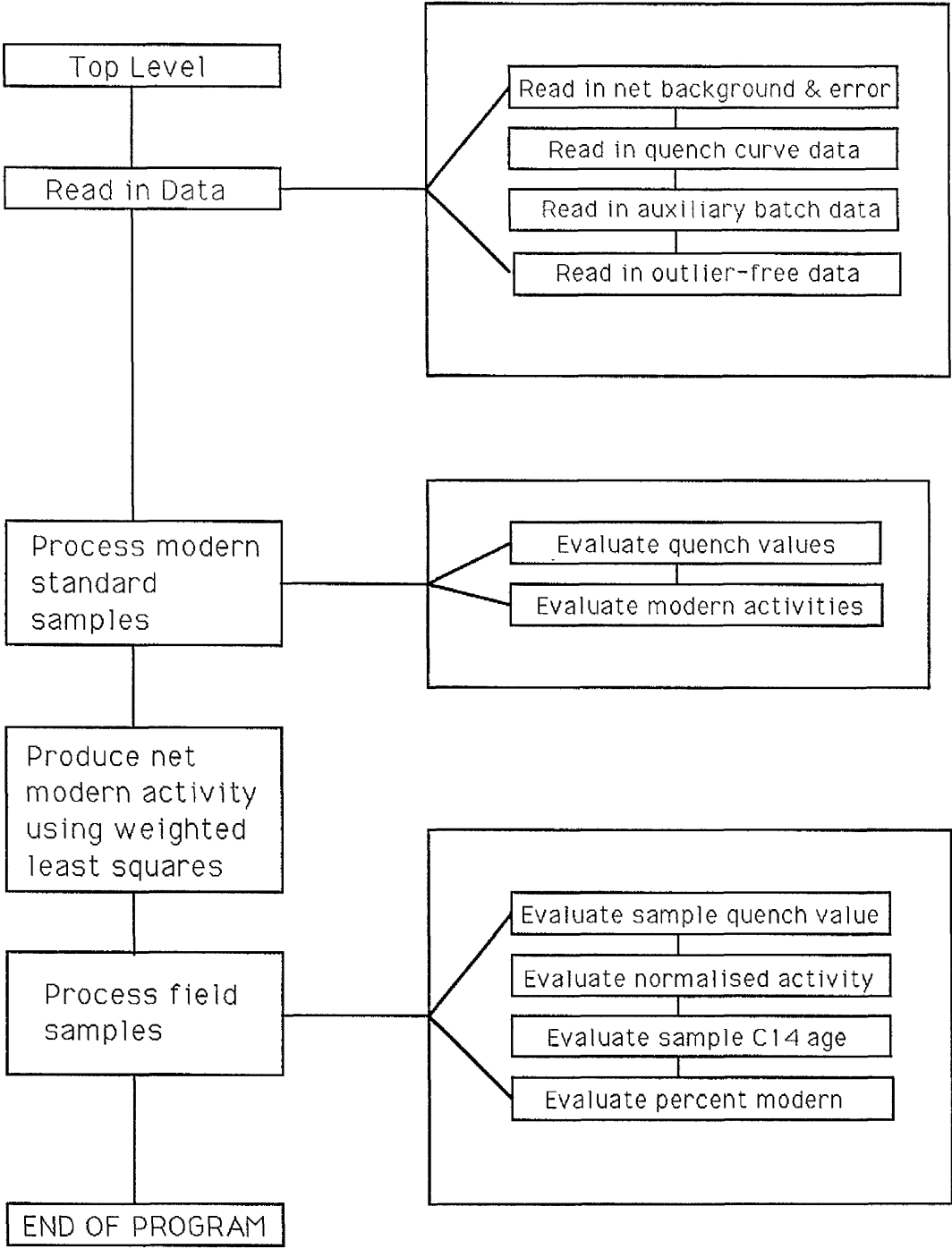
7.2 Description of the Age Program

The age program is a much more flexible program compared to the outlier program. For a start, there is no limit this time to the size of samples which may be handled by this program. None of the statistical algorithms contained in the age program are restricted to only work with a limited number of samples and/or sample observations.

The program is presented in Appendix B and, as mentioned before, routines shared with the outlier program appear in Appendix C. Figure 7.2 provides a useful illustrative summary of the age program, outlining the nature and order of program tasks.

There are three main tasks after all the relevant data has been read in by the program.

Figure 15: illustration of age program



The first of these main tasks is the evaluation of quench values and modern activities for each modern standard sample in the batch. The modern activities are simply the normalised standard activities times the appropriate multiplicative factor which produces conformity to the primary wood standard. This can be written as $\hat{\theta}_m = k \hat{\theta}_{ox}$ where $\hat{\theta}_m$ is the estimate of the modern activity and is equal to the appropriate multiplicative factor k times the estimate of the normalised standard activity $\hat{\theta}_{ox}$. The second main task is to calculate a mean modern activity derived from all standard samples by using weighted least squares with covariances. The mean modern activity is just k times the mean standard activity. An estimate and error for the latter statistic are defined, respectively, in equations (E5.1) and (E5.2). The third main task is the evaluation of four statistics for each field sample: the sample quench value, the normalised sample activity, the percent modern and the radiocarbon age. Each of these statistics is evaluated with a corresponding error.

7.2.1 Analysis of Age Program Routines

The age program is comprised of 17 routines, 5 of which it shares with the outlier program. The descriptions of the routines follow the same pattern as before with emphasis on the main variables assigned in each routine. The program routines (those marked [†] appear in Appendix C) are :-

(1) AGE *Main Assigned Variable(s):* NONE.

Top level routine which regulates the various tasks to be performed by the age program.

- (2) BLOCK1[†] See comment in program.
- (3) BLOCK2[†] See comment in program.
- (4) INBACK *Main Assigned Variable(s):* REAL BACK;
REAL ERRBK.

A prompt appears on the screen:

PLEASE TYPE IN BACKGROUND MEAN :

The operator responds by typing in the batch background activity (format F6.3) which will only be known once the outlier program has been run and the report from that program has been read. When a value for the background activity has been received and stored in BACK, a second prompt appears on the screen:

PLEASE TYPE IN BACKGROUND ERROR:

The operator types in the value (format F6.3) and once a value has been received it is stored in ERRBK.

- (5) INAXI[†] See description in outlier program.

(6) INQUEN

Main Assigned Variable(s): REAL A,B,C;

REAL V1,V2,V3,V4,V5,V6;

REAL BSIE,SDFIT,DIV.

The quench curve data is read in from the appropriate file. This curve is constructed from an independent series of spiked (high count) samples. These samples are spiked using small amounts of acetone. Before quenching, all of the samples possess an equal activity close to 4000 disintegrations per minute per gram (dpm/g). After quenching, the samples are counted and their sie values recorded. The observed counting activities (cpm/g) are then regressed on the sie values (scaled down to prevent complexities in calculation — see below) for the whole quenched series which includes an unquenched standard. The best regression function here is a simple quadratic polynomial since the counting efficiency appears to fall away symmetrically and with slowly increasing gradient on either side of some critical sie value, this latter value being related to some critical level of quenching. This can be informally explained: the pulse amplitudes which are measured over the counting window will tend to disappear into the lower and higher unseen energy regions on either side of the counting window according to the particular side of the critical sie value a sample falls. A baseline sie value is chosen which should be reasonably close to the critical value. (The exact value is not essential since quench correction is a relative correction and not an absolute one.) The idea is to normalise the counting activities of samples relative to this baseline, that is, to correct for slight variations in counting efficiency by adjusting the counting activities of samples to those of

definitions can be given here which conform to those definitions appearing in section 5.6.2 :-

$$\begin{aligned}
 \text{VECTOX}^T &= (o_{11}^* \dots o_{1n_1}^* \vdots \dots \vdots o_{k1}^* \dots o_{kn_k}^*) \\
 \text{VECVAR}^T &= (\underbrace{\sigma_1^{-2} \dots \sigma_1^{-2}}_{n_1} \vdots \dots \vdots \underbrace{\sigma_k^{-2} \dots \sigma_k^{-2}}_{n_k}) \\
 \text{GAMMOX}^T &= (\underbrace{\gamma_1^{-1} \dots \gamma_1^{-1}}_{n_1} \vdots \dots \vdots \underbrace{\gamma_k^{-1} \dots \gamma_k^{-1}}_{n_k}) \\
 \text{GAMVAR}^T &= (\underbrace{\tau_1^2 \dots \tau_1^2}_{n_1} \vdots \dots \vdots \underbrace{\tau_k^2 \dots \tau_k^2}_{n_k}) \\
 \text{NOX}^T &= (n_1 \ n_2 \ \dots \ n_k)
 \end{aligned}$$

The age program presently caters for a maximum of 6 standard samples in any one batch each possessing a maximum of 12 observations — this accounts for the size of the first four arrays above, namely $72 = 6 \times 12$. These values may be altered to any values within reasonable limits.

- (9) QUVALU *Main Assigned Variable(s):* NONE.

A quench correction value and error are evaluated for a sample (see QCURVE below).

- (10) VALUES[†] See description in outlier program.

- (11) QCURVE *Main Assigned Variable(s):* REAL QUENCH;
REAL ERRQU.

See INQUEN for definitions of variables cited here. An average sie value is evaluated for a sample and scaled down by dividing by DIV. The value of DIV must match the value employed in the regression (DIV currently assumes a value

of 1000.0 since this makes the quench calculations a lot easier). The average sie value is subsequently referred to the regression equation derived from the quenched series in order to obtain an estimate of the activity — belonging to the order of 4000 dpm/g — which would be expected for a sample possessing such an sie value. This expected activity is then divided into the expected activity of the baseline sie value (scaled down, namely BSIE/DIV) and the resultant ratio constitutes the quench correction factor for the sample. This standardises all activities to a common and hopefully near optimal counting efficiency. It would be useful here to show the estimation of the quench correction factor in statistical terms. Let Y be the expected activity (around 4000 dpm/g) of a sample possessing an sie value X . The former value is obtained from the latter according to the regression equation $Y = b^T \hat{\alpha}$ where $b^T = (1 \ X \ X^2)$ and $\hat{\alpha}^T = (A \ B \ C)$, the vector of the estimated coefficients of the quadratic fit. Plugging in X_{base} and X_{sample} into the regression equation produces, respectively, Y_{base} and Y_{sample} . The quench value (QUENCH) is then simply given by

$$q = \frac{Y_{\text{base}}}{Y_{\text{sample}}}$$

A standard error for q is now obtained. The error of any expected activity Y pertaining to an sie value X is

$$\sigma(Y) = \sigma(b^T \hat{\alpha}) = \sqrt{\frac{\text{RSS}}{(n-3)}} \times \sqrt{b^T (A^T A)^{-1} b}$$

where RSS is the residual sum of squares for the fitted curve, n is the number of samples in the quenched series used to construct the curve and the matrix

$(A^T A)^{-1}$ is the matrix whose elements are V1-V6, i.e. the inverse covariance matrix of the regression. (The value of 3 is removed from n due to the 3 estimated coefficients of the quadratic fit.) The value of $\sqrt{RSS/(n-3)}$ is equal to the value which is stored in SDFIT. Errors are evaluated for both Y_{base} and Y_{sample} using the above equation and the error of q is

$$\text{ERRQU} = \text{SDFIT} \times \sqrt{\frac{[\sigma(\mathbf{y}_{\text{base}})]^2}{\mathbf{y}_{\text{base}}^2} + \frac{[\sigma(\mathbf{y}_{\text{sample}})]^2}{\mathbf{y}_{\text{sample}}^2}}$$

```
(12) ACTVTY           Main Assigned Variable(s): REAL ACTIV;
                                     REAL ERRAC.
```

The normalised activity of a sample is calculated. According to the convention adopted throughout this report, this is the same calculation for both modern standard and field samples. (The normalised activity of modern standard samples is multiplied by the appropriate multiplicative factor in the OXALIC routine to obtain the modern activity.) The normalised activity (ACTIV) is the average sample cpm value corrected for background times the sample gamma value (defined in OXALIC). The error of the normalised activity is

$$\text{ERRAC} = \text{ACTIV} \times \sqrt{\frac{\sigma_{ac}^2 + \sigma_{mb}^2}{(\text{ac} - \text{mb})} + \frac{\sigma_q^2}{q^2}}$$

where ac is the average sample cpm value, mb is the mean background activity and q is the quench correction factor. This is the same error as the one presented in section 5.5.1 (see step 2 of the calculation of the error of age).

(13) **AVSTAN**[†] See description in outlier description.


```

(14) OXMEAN           Main Assigned Variable(s):  DIMENSION AOX1(72);

                                                           DIMENSION AOX2(72);

                                                           REAL U,V;

                                                           REAL OXNET,ERROX;

                                                           REAL OXNETF,ERROXF.

```

An estimate is obtained for the modern activity derived from all standard samples in the batch under process. The estimation requires knowledge of the form of the inverse covariance matrix of standard cpm values corrected for background, namely Σ_{ϕ}^{-1} according to the notation appearing in section 5.6.2. It is recalled that $\Sigma_{\phi} = M_{ox} + M_b$ where M_{ox} is the diagonal matrix whose diagonal elements are the variances of the standard cpm values and M_b is the square matrix whose elements are all equal to the variance of the mean background activity. The matrix Σ_{ϕ}^{-1} thus possesses a highly convenient form since the inverse of this form of matrix — general form $M_{n \times n} = D_{n \times n} + b \mathbf{1}_n^T \mathbf{1}_n$ where matrix $D_{n \times n}$ is diagonal — has known form $b^* M_{n \times n}^*$ where $b^* = (\sum_{i=1}^n D_{ii} + b^{-1})^{-1}$, $M_{ii}^* = D_{ii} - D_{ii}^2/b^*$ and $M_{ij}^* = -D_{ii}D_{jj}/b^*$, $i \neq j$ (the $\{D_{ii}\}$ and the $\{M_{ii}\}$ are the diagonal elements of $D_{n \times n}$ and $M_{n \times n}^*$, respectively, and the $\{M_{ij}^*\}$ are the off-diagonal elements of $M_{n \times n}^*$). The OXMEAN routine first estimates the mean modern activity. Several intermediate variables are assigned values in the process of estimating the mean modern activity: these are $AOX1 = \Sigma_{\phi}^{-1} \phi$, $AOX2 = \Sigma_{\phi}^{-1} \pi$, $U = \pi^T \Sigma_{\phi}^{-1} \phi$ and $V = \pi^T \Sigma_{\phi}^{-1} \pi$ according to the notation which appears in section 5.6.2. This allows evaluation of the mean standard activity which is simply given by $OXNET = U/V$ in accordance with equation (E5.1) and

this in turn gives the mean modern activity $OXNETF = \text{FACTOR} \times OXNET$ (the multiplicative term **FACTOR** assumes the appropriate value defined in the block data subprogram **BLOCK2**). The **OXMEAN** routine now evaluates an error for the mean modern activity which is given by $ERROXF = \text{FACTOR} \times ERROX$ where **ERROX** is the error of the mean standard activity defined according to equation (E5.2).

(15) FIELDS *Main Assigned Variable(s):* NONE.

Four statistics are evaluated for each field sample: the sample quench value, the normalised sample activity, the sample percent modern and the sample radiocarbon age.

```
(16) AGESMP      Main Assigned Variable(s):  INTEGER IAGE;
                                           INTEGER IERRAG;
                                           REAL COV.
```

The radio carbon age of a sample is evaluated. It is rounded to the nearest integer (IAGE) and the error of the age is rounded up to an integer (IERROR). A covariance term (COV) is also evaluated which arises from the covariances between the standard cpm values corrected for background and the field sample cpm values corrected for background. The covariance term is required in the calculation of the error of the percent modern as well as in the calculation of the error of the age. The estimates of age and error of age conform to those in equation (E5.9).

(17) PERSMP

Main Assigned Variable(s): REAL PERCNT;

REAL ERRPC.

The sample percent modern is evaluated. This is the percent ratio of the normalised field sample activity over the mean modern activity. It is very closely related to the estimated sample age since

$$\text{PERCNT} = 100 \times \hat{\theta}_m^{-1} \hat{\theta}_s = 100 \times e^{-\lambda \hat{t}}$$

where $\hat{\theta}_s$ is the estimated field sample activity, $\hat{\theta}_m$ is the estimated modern activity, \hat{t} is the estimated sample age and λ is the age constant. The percent modern is straightforwardly estimated since the normalised field sample activity and the mean modern activity are already available. The error of the percent modern is given by

$$\text{ERRPC} = \text{PERCNT} \times \sqrt{\frac{\text{ERROX}^2}{\text{OXNET}^2} + \frac{\text{ERRAC}^2}{\text{ACTIV}^2} - \frac{2 \times \text{COV}}{\text{OXNET} \times \text{ACTIV}}}$$

where OXNET and ERROX are the mean standard activity and error, ACTIV and ERRAC are the normalised sample activity and error and COV is the covariance termed which is calculated in the AGESMP routine. A proof for the above error is not presented here but it is very similar to proof (P5.8) pertaining to the error of the sample age. The inclusion of the covariance term is for the sake of consistency and also provides greater accuracy in the specification of error. The percentage reduction gained in the error of the percent modern by taking into account covariances due to background corrections would be approximately the same as that gained for the error of the sample age since the two errors are

closely related.

This completes the descriptions of the age program routines. These descriptions should assist in the understanding of the program.

7.2.2 Limitations of the Age Program

It is important to recognise that the age contains certain features which affect its generability.

There are at least three such features :-

- (a) *The estimation of the quench correction factor.* The age program's evaluation of a quench value may be entirely peculiar to the East Kilbride laboratory. It is unlikely that every detail of the method here is identically reproduced by another laboratory although there may exist other methods which are closely related. This means that modifications of some sort would be required to be undertaken in order to adapt the program to another environment. Any such modifications would affect the INQUEN and QCURVE routines depending on how quench correction is to be applied to the counting data.
- (b) *No test for bias among modern standard samples.* The absence of such a test is due to the complexity of the equations (E5.6) pertaining to the estimates under the alternative hypothesis in the test of bias, particularly the Λ and Ω matrices. The memory limitations of the computer also prevent the test from being installed for the moment but in future with a more powerful computer system the test will hopefully be incorporated into the software once a suitable way of computing the Λ and Ω matrices

has been found. (The author is presently considering possible algorithms for inverting matrices on the computer.)

- (c) *The use of an oxalic standard.* Although the program was written with the oxalic standard in mind as indicated by the names of some of the routines (e.g. OXALIC) and by some of the comments in the program, it is not completely constrained to work with that standard only. With minor modifications to the routine names/comments and to the value assigned to the FACTOR variable, it may be quite easily modified to work with any standard.

Only the first of the above features constitutes a serious limitation and even there it is possible to salvage something. This means that the age program is likely to be a more flexible program than the outlier program. This leaves us to briefly examine the input/output files connected with both programs.

7.3 Descriptions of Input/Output Files

There are three input files, two output files and one file which is both an input and an output file. These files are listed in Table 13. Files (1)–(4) in this table are data files and files (5) and (6) are the reports generated by each of the programs. It is useful to examine the files separately with respect to this distinction.

The data formats of each data file are listed in Table 14. The format of the outlier-free data file is of no real interest since it is an ‘invisible’ file passed between the outlier program and the age program. The data in that file are equivalent to the data in the main unprocessed data file except that outliers are removed from the former data. The data format of the main

File	Type	Program Link(s)	Name
(1) Auxiliary Batch Data	I	Outlier/Age	AUXIDATA.DAT
(2) Quench Curve Data	I	Age	QUENDATA.DAT
(3) Main Unprocessed Data	I	Outlier	ORIGDATA.DAT
(4) Outlier-free Data	I/O	Outlier(O)/Age(I)	PUREDATA.DAT
(5) Outlier Report	O	Outlier	OUTLIERS.REP
(6) C14 Ages Report	O	Age	C14-AGES.REP

Table 13: The input/output files connected with the outlier and age programs where type I=input, type O=output and the file names are those appearing in block data subprogram BLOCK2 in Appendix C.

Data File	Data Format
Auxiliary Batch	F3.0,1X,A1,1X,F5.0,1X,F5.3,1X,F6.4
Quench Curve	6X,F12.3
Main Unprocessed	7X,F3.0,F7.2,26X,F8.0,5X,F5.0
Outlier-free	F3.0,1X,F7.2,1X,F8.0,1X,F5.0

Table 14: data formats of all relevant data files.

unprocessed data has one quirk worth mentioning: there is an invisible line-feed character at the beginning of each data line generated by the Packard counter on the Apple system (it does not appear on the first data line but this is not upsetting since the initial lines in this data file are not essential data lines). The invisible character can be entirely ignored whenever a data conversion (e.g. 'F6.3', 'A15', 'I4', etc.) is applied to the very beginning of an input data line but with respect to the present data file the first operation on the data line is not a data conversion but rather the skipping of characters, represented in the data format specification by '7X'. The '7X' only skips 6 physical characters in the actual data lines because it takes into account the invisible character at the beginning of the lines. This may just be a quirk of the Apple system and may not be applicable in other systems.

The other two data files, namely the auxiliary batch and quench curve data files, need

to be written manually by the system operator before the programs are run. The auxiliary batch data file has the same number of data lines as the number of samples in the batch which is to be processed and the first seven data lines from an imaginary file possessing the relevant data format could look like

```
01. B 0264. 0.000 0.0000
02. M 0148. 4.491 1.0022
03. G 5307. 2.985 0.9994
04. G 5308. 4.503 0.9998
05. G 5309. 4.499 1.0045
06. B 0265. 0.000 0.0000
07. M 0149. 4.500 1.0001
```

The description of the INAXI routine belonging to the outlier program identifies each of the columns in this data file.

The quench curve data file has exactly 12 data lines at the present time. A typical quench curve data file might look like

```
DUMMY
A      =-1629.1
B      =15298.9
C      =-11327.5
V1     =55.148
V2     =-179.581
V3     =142.588
V4     =588.256
V5     =-469.893
V6     =377.840
BASE   =600.0
SD      =17.14
DIV     =1000.0
```

The inclusion of a dummy line in the data file is to circumvent the problem of the invisible

character not appearing in the first data line. This is not a problem with the auxiliary batch data file because a number conversion is performed at the beginning of data lines but here the program is required to skip the first 5 physical characters of data lines — these 5 characters are used as comments to identify the variables — and so the format needs to begin with '6X' in order to include the invisible character. (The author apologises if this is all a little bit confusing but the pain of working with this system was bound to result in a measure of confusion.) The variables listed in the quench curve data file above can be identified by consulting the description of the INQUEN routine belonging to the age program.

The two program reports remain to be finally examined. An example of the outlier program report is provided in Appendix D and an example of the the age program report is provided in Appendix E. These examples are based on a real data set containing 20 samples made up of 5 background samples (B), 4 modern standard samples (M), 10 field samples (G) and 1 spiked sample (S). The reports are fairly self-explanatory except to say that the detected outliers in the outlier program report were due to corruptions in the data file which occurred during the transference of the data from one physical location to another. The contents of both reports are the products of the statistical algorithms which have been outlined in the descriptions of the routines of both programs. These descriptions should be consulted for any clarification which may be required in the reading of the program reports.

8 Conclusions and Future Work

The work of this study is clearly only a beginning of sorts and is far from being complete. It has been an attempt in its most general sense to introduce a selected number of statistical quality controls into the management of carbon-14 counting data. Some of these controls are perhaps too specific to the East Kilbride laboratory to have general application but hopefully some of this work will have a wider application than one laboratory.

This last section is in two parts: first, an overview of what has been achieved; second, a brief survey of work still to be done, some of which the author hopes to accomplish through continuation of research at East Kilbride.

8.1 Assessment of the Work Done So Far

A foundation has at least been laid down which allows further work to be built upon it. The software presently incorporates some basic statistical features alongside features which were developed during the course of this study.

In section 2 a limited correlation study was conducted which revealed nothing unusual in the counting data of some background samples. The results, however, would not support any sweeping statements which could be made about other types of samples nor establish that time trends are absent from the data. The data as it stands does not facilitate proper tests of time trends and significant trends are unlikely to manifest within the relatively small time period of a single batch. In the same section a study of the normality of background counting data proved positive and simply confirmed prior expectations.

An outlier test was developed in section 3 and incorporated into the software. This

test is limited inasmuch as it was designed for small samples due to the present computer limitations. The test, though, has proved its worth for small samples in the running of the outlier program over several years but it is currently being reviewed with respect to the proposed merging of the counting data of batches to form one large data set as an alternative to the pooling of separate batch statistics. The small sample outlier test will still be retained, however, since ten cycle batches are still going to be processed in order to conduct running checks on samples so that irregular samples may be detected and discarded sooner rather than later.

The evaluation of the mean background activity was examined in section 4. A new approach to estimation was devised in the form of the retrospect estimate of the background activity where the idea was to align background samples to a common standard defined within the samples themselves and according to the history of the samples. The complications of the method, including the refinement of its definition, however, has meant that the method still remains in its conceptual state.

More practical progress was made in sections 5 and 6 where an alternative method was found of estimating the mean standard activity which uses weighted least squares taking into account correlation in the counting data subsequent to corrections for background. The result was an 8.5% error reduction for 4 modern standard samples belonging to a 10 cycle counting series and 16.6% for the same number of samples belonging to a 60 cycle counting series (6 batches each 10 cycles long). This result needs to be treated with a little caution. The problem relating to the fact that some laboratories may already be underestimating their internal variability would only be compounded if those laboratories adopted the alternative age estimator without some sort of suitable error multiplication.

Also, the percentage reductions in error that were observed may largely be a consequence of empirical, rather than theoretical, properties and this would need to be considered by any potential user of the age estimator to determine its usefulness in other data contexts.

Finally, the programs themselves are the culmination of the work and were presented in the previous section. They have been modularised in such a way as to facilitate effective alteration/extension/removal of the various program routines which may need to be carried out in the maintenance and updating of the programs. The real extent of their generability can only be ascertained by other laboratories themselves.

8.2 What Next?

There is much scope to continue the work. The intended aggregation of the counting data at East Kilbride leaves room for further research. The recent introduction of the new IBM computer system in the laboratory is hopefully going to help in the extension of the software. A number of new features to be included in the software are being considered at the present time :-

- It is desired to merge the outlier and age programs into one program. This would be an improvement in the sense that a second outlier-free data file would not be required to be generated, eating up disk space to a greater extent if the data set is to be enlarged. It also means that the system operator does not need to examine the outlier report before typing in the value of the background and error since this would be done internally within the one program.

These suggestions for future work might be supplemented at a later stage by other ideas which may occur in the process of developing the software but at least they provide a basis for aiming toward even better management of carbon-14 counting data.

- Tests of bias among background and modern standard samples are needed to provide better quality control. The test for the background samples is relatively straightforward and the test for standard samples is already defined in this report and only requires translation into some appropriate software.
- A test for multiple outliers is a top priority requirement. The small sample outlier test will be retained for the purpose of analysing the 10 cycle batches which will still require analysis even although they will eventually be combined when a series of batches is completed. The tests for multiple outliers which are briefly discussed in section 3 provide scope for devising and implementing a multiple outlier detection method.
- The larger data set would facilitate proper time trend tests. It is not clear what precise tests would be employed but the idea of employing tests of time trends would generally be considered favourable.
- It would also be a good idea to consider the possibility of incorporating statistical graphs into the software. The quality control graphs suggested by Switzur would be ideal but this is dependent on what graphics facilities are available at East Kilbride. (This is not known by the author at the present moment.)
- Array sizes would generally be increased once the statistical algorithms have been suitably adapted to the larger data context.
- On a minor point, the use of the protocol number generated by the Packard counters could be put to better use. The program could be changed to accommodate a different use of that number.

C** (5) 'AVSTAN' (S) — CALCULATES MEAN AND STANDARD ERROR
C** FOR AN ARRAY OF VALUES.
C**

C** NOTE: MORE DETAILED DESCRIPTIONS, INCLUDING DESCRIPTIONS OF
C** MAIN VARIABLES, ARE PROVIDED IN THE COMMENTS APPEARING AT THE
C** BEGINNING OF EACH ROUTINE.
C**
C**

PROGRAM OUTLIE

C**
C**
C** MAIN PROGRAM ROUTINE FOR :-
C** (1) DETECTING OUTLIERS IN DATA;
C** (2) CALCULATING SAMPLE MEANS;
C** (3) ESTIMATING BACKGROUND LEVEL BY
C** POOLING OF BACKGROUND SAMPLES.
C** NOTE: THE VARIABLES IN THIS MAIN ROUTINE ARE DESCRIBED
C** AND INITIALISED IN THE BLOCK DATA SUBPROGRAM 'BLOCK1'
C** WHICH IS CURRENTLY LOCATED IN THE FILE 'SHARED.FOR'.
C**
C**

EXTERNAL BLOCK1, BLOCK2
INTEGER DRIVE, OUT, UNIT1, UNIT2, UNIT3, UNIT4
REAL*8 FILE1(2), FILE2(2), FILE3(2)
REAL*8 FILE4(2), FILE5(2), FILE6(2)
LOGICAL LF
COMMON /DISK/ DRIVE
COMMON /FILE/ FILE1, FILE2, FILE3, FILE4, FILE5, FILE6
COMMON /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
COMMON /CHAR/ LF

C**
C**
C** OPEN ALL INPUT AND OUTPUT FILES. THE RELEVANT FILES ARE :-
C** (1) AUXILIARY DATA FILE (INPUT FILE='FILE1');
C** (2) UNPROCESSED DATA FILE (INPUT FILE='FILE3');
C** (3) OUTLIER-FREE DATA FILE (OUTPUT FILE='FILE4');
C** (4) OUTLIER REPORT FILE (OUTPUT FILE='FILE5').
C**
C**

CALL OPEN(UNIT1, FILE1, DRIVE)
CALL OPEN(UNIT2, FILE3, DRIVE)
CALL OPEN(UNIT3, FILE4, DRIVE)
CALL OPEN(UNIT4, FILE5, DRIVE)

C**
C**
C** BEGIN PROCESSING :-
C** (1) 'OQUERY' QUERIES OPERATOR ABOUT OPTION TO DELETE
C** BACKGROUND SAMPLES — SEE (3) BELOW;
C** (2) 'INAXI' READS IN AUXILIARY BATCH DATA (FILE='FILE1');
C** (3) 'OPTION' ALLOWS BACKGROUND SAMPLES TO BE DELETED FROM

```

C**          THE BATCH ESTIMATE OF THE BACKGROUND LEVEL;
C**          (4) 'INDATA' READS IN UNPROCESSED BATCH DATA (FILE='FILE3');
C**          (5) 'OUTDET(1,...)' SEARCHES FOR OUTLIERS AMONG SAMPLE
C**              COUNTS;
C**          (6) 'OUTDET(2,...)' SEARCHES FOR OUTLIERS AMONG SAMPLE
C**              SIE VALUES;
C**          (7) 'NEWDAT' WRITES OUTLIER-FREE DATA TO THE APPROPRIATE
C**              OUTPUT FILE (FILE='FILE4');
C**          (8) 'AVRAGE(...)' CALCULATES MEANS FOR DATA;
C**          (9) 'BACKGR(...)' ESTIMATES BACKGROUND LEVEL BY POOLING
C**              OF BACKGROUND SAMPLES.
C**          NOTE: (5), (6), (8) AND (9) EACH REPORT TO THE SAME OUTPUT
C**          FILE (FILE='FILE5').
C**

```

```

KOUNT=0
CALL OQUERY
CALL INAXI
CALL OPTION
CALL INDATA
CALL OUTDET(1, KOUNT)
CALL OUTDET(2, KOUNT)
CALL NEWDAT
CALL AVRAGE(KOUNT)
CALL BACKGR(KOUNT)
WRITE(UNIT4,2038) LF,LF,LF,LF,LF,LF,LF,LF
WRITE(OUT,2039)
STOP

```

```

C**
C**
2038  FORMAT(A1/A1/A1/A1/A1/A1/A1,'+++ END OF REPORT +++')
2039  FORMAT(/3X,'+++ END OF PROGRAM +++'//)
END

```

SUBROUTINE OQUERY

```

C**
C**
C**          THIS SUBROUTINE QUERIES THE OPERATOR CONCERNING THE
C**          OPTION TO DELETE BACKGROUND SAMPLES FROM THE BATCH
C**          ESTIMATE OF THE BACKGROUND LEVEL.
C**
C**

```

```

INTEGER      OUT, UNIT1, UNIT2, UNIT3, UNIT4
INTEGER      BDLETE(6)
LOGICAL      YES, NO, REPLY, DELETE
COMMON       /OPTN/ DELETE, BDLETE, NDLETE
COMMON       /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
DATA         YES, NO /'Y', 'N'/

```

```

C**
C**
256  WRITE(OUT,2038)
      READ(IN,1006) REPLY

```

```

      IF (REPLY.EQ.YES.OR.REPLY.EQ.NO) GOTO 257
      WRITE(OUT,3007)
      GOTO 256
257  IF (REPLY.EQ.NO ) DELETE=.FALSE.
      IF (REPLY.EQ.YES) DELETE=.TRUE.
      RETURN
C**
C**
1006  FORMAT(A1)
2038  FORMAT(/3X,'DO YOU WANT THE OPTION TO DELETE? (Y/N):')
3007  FORMAT(/3X,'*** UNKNOWN REPLY ***  TYPE "Y" OR "N" ONLY.')
```

END

SUBROUTINE OPTION

```

C**
C**
C**      THIS SUBROUTINE ALLOWS DELETION OF BACKGROUND SAMPLES FROM THE
C**      BATCH ESTIMATE OF THE BACKGROUND LEVEL. (NOTE: THE STATISTICS
C**      FOR ANY DELETED BACKGROUND SAMPLE WILL STILL BE REPORTED.)
C**      THE OPERATOR MUST TYPE IN THE INTEGER CODE OF ANY BACKGROUND
C**      SAMPLE WHICH IS TO BE DELETED. THIS CODE MUST MATCH THE CODE
C**      ASSIGNED TO THE RELEVANT BACKGROUND SAMPLE IN THE AUXILIARY
C**      BATCH DATA FILE. THE CODES FOR DELETED BACKGROUND SAMPLES ARE
C**      STORED IN THE 'BDLETE' ARRAY AND THE NUMBER TO BE DELETED IS
C**      RECORDED IN 'NDLETE'. THE SYMBOL FOR BACKGROUND SAMPLES FOUND
C**      IN 'BKTYPE' IS SPECIFIED IN THE BLOCK DATA SUBPROGRAM 'BLOCK2'.
C**
C**
      INTEGER      OUT, UNIT1, UNIT2, UNIT3, UNIT4
      INTEGER      BDLETE(6)
      LOGICAL      YES, NO, REPLY, DELETE, MATCH
      LOGICAL      BKTYPE, OXTYPE, FSTYPE, TYPE(30)
      DIMENSION    DATA(360,4), BATCH(30,4)
      COMMON       /INFO/ DATA, BATCH, TYPE
      COMMON       /OPTN/ DELETE, BDLETE, NDLETE
      COMMON       /TYPN/ BKTYPE, OXTYPE, FSTYPE
      COMMON       /VARS/ MODE, NDATA, NBATCH
      COMMON       /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
      DATA        YES, NO /'Y', 'N'/
C**
C**
      IF (.NOT.DELETE) GOTO 213
      IX=0
203  WRITE(OUT,2002)
      READ(IN,1002) REPLY
      IREPLY=-1
      IF (REPLY.EQ.NO ) IREPLY=0
      IF (REPLY.EQ.YES) IREPLY=1
      IF (IREPLY) 208,207,204
204  WRITE(OUT,2003)
      READ(IN,1003,ERR=209) KODE
      IF (KODE.EQ.0) GOTO 210

```

```

C**
C**
C**      CHECK THAT CODE MATCHES EXISTING BACKGROUND SAMPLE CODE.
C**
C**      MATCH=NO
          DO 205 NX=1,NBATCH
205      IF (BATCH(NX,2).EQ.KODE.AND.TYPE(NX).EQ.BKTYPE) MATCH=YES
          IF (MATCH.EQ.NO) GOTO 211
C**
C**
C**      CHECK THAT CODE HAS NOT ALREADY BEEN RECEIVED.
C**
C**
C**      MATCH=NO
          DO 206 NX=1,IX
206      IF (BDLETE(NX).EQ.KODE) MATCH=YES
          IF (MATCH.EQ.YES) GOTO 212
C**
C**
C**      IF CODE ACCEPTABLE THEN RECORD IT FOR DELETION.
C**
C**
C**      IX=IX+1
          BDLETE(IX)=KODE
          WRITE(OUT,2004)
          GOTO 203
C**
C**
C**      IF NO (FURTHER) DELETIONS REQUIRED THEN EXIT ROUTINE.
C**
C**
207      NDLETE=IX
          GOTO 213
C**
C**
C**      MESSAGES TO THE SCREEN (MAINLY ERROR MESSAGES).
C**
C**
208      WRITE(OUT,3001)
          GOTO 203
209      WRITE(OUT,3002)
          GOTO 204
210      WRITE(OUT,3003)
          GOTO 203
211      WRITE(OUT,3004)
          GOTO 204
212      WRITE(OUT,3005)
          GOTO 203
213      RETURN
C**
C**
1002     FORMAT(A1)
1003     FORMAT(I5)
2002     FORMAT(/3X,'DO YOU WANT TO DELETE ANY BACKGROUND SAMPLE'

```

```

&      /3X,'FROM THE OVERALL ESTIMATE OF BACKGROUND? (Y/N):')
2003  FORMAT(/3X,'TYPE IN BACKGROUND SAMPLE CODE (0 TO EXIT):')
2004  FORMAT(/3X,'CODE RECEIVED. OPTION TO DELETE STILL OPEN ...')
3001  FORMAT(/3X,'*** UNKNOWN REPLY ***  TYPE "Y" OR "N" ONLY.')
```

```

3002  FORMAT(/3X,'*** CODE MUST BE INTEGER ***  PLEASE TYPE AGAIN.')
```

```

3003  FORMAT(/3X,'*** EXIT CODE RECEIVED ***  OPTION STILL OPEN.')
```

```

3004  FORMAT(/3X,'*** NO MATCH FOR CODE ***  PLEASE TYPE AGAIN.')
```

```

3005  FORMAT(/3X,'*** CODE ALREADY RECEIVED ***  OPTION STILL OPEN.')
```

```

END
```

SUBROUTINE INDATA

```

C**
C**
C**      THIS SUBROUTINE READS IN THE UNPROCESSED BATCH DATA.
C**      FOUR ITEMS ARE READ IN FROM EACH DATA RECORD.
C**      THESE ITEMS ARE :-
C**          (1) SAMPLE NUMBER;
C**          (2) SAMPLE COUNTING TIME;
C**          (3) SAMPLE GROSS COUNT VALUE;
C**          (4) SAMPLE SIE VALUE.
C**      A DATA RECORD IS ONLY ACCEPTED HERE IF THE 'NTH'
C**      CHARACTER IN THE RECORD IS EQUAL TO THE PROTOCOL
C**      NUMBER DENOTED BY 'PRONUM' — THIS PERTAINS TO
C**      THE WAY THAT THE COUNTER WRITES THE DATA. 'NTH'
C**      AND 'PRONUM' ARE SPECIFIED IN THE BLOCK DATA
C**      SUBPROGRAM 'BLOCK2'.
C**      THE DATA IS STORED IN THE 'DATA' ARRAY AND THE
C**      NUMBER OF DATA RECORDS IS RECORDED IN 'NDATA'.
C**
C**
C**      INTEGER      OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      LOGICAL      LF, PRONUM, RECORD(80), TYPE(30)
C**      DIMENSION    DATA(360,4), BATCH(30,4)
C**      COMMON       /INFO/ DATA, BATCH, TYPE
C**      COMMON       /VARS/ MODE, NDATA, NBATCH
C**      COMMON       /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      COMMON       /CHAR/ LF
C**      COMMON       /PNUM/ PRONUM, NTH
C**
C**
C**      WRITE(OUT,2005)
C**      NR=0
214  READ(UNIT2,1004,END=215) (RECORD(I),I=1,80)
      IF (RECORD(NTH).NE.PRONUM) GOTO 214
      NR=NR+1
      DECODE(RECORD,1005) (DATA(NR,J),J=1,4)
      GOTO 214
215  NDATA=NR
      IF (NDATA.EQ.0) GOTO 315
      WRITE(OUT,2006)
      GOTO 316
315  WRITE(OUT,3006)
```

```

316  STOP
    RETURN
C**
C**
1004  FORMAT(80A1)
1005  FORMAT(7X,F3.0,F7.2,26X,F8.0,5X,F5.0)
2005  FORMAT(/3X,'READING PRIMARY DATA FILE ...')
2006  FORMAT(3X,'DATA RECEIVED.'/)
3006  FORMAT(/3X,'*** DATA FILE EMPTY ***  PROGRAM STOPPED.'//)
    END

SUBROUTINE  OUTDET(MODEX, KOUNT)

C**
C**
C**      THIS SUBROUTINE SEARCHES FOR OUTLIERS AMONG ALL
C**      SAMPLES. THE 'MODE' VARIABLE DETERMINES WHICH SAMPLE
C**      OBSERVATIONS ARE TO BE PROCESSED — COUNTS ('MODE'=1)
C**      OR SIE VALUES ('MODE'=2).
C**      THE LOGICAL ARRAY 'CLEAR' IS USED HERE TO DETERMINE
C**      IF THE SAMPLES ARE CLEAR OF OUTLIERS OR NOT.
C**
C**      INTEGER      RUN, SUM, OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      LOGICAL      LF, CLEAR(30), TYPE(30)
C**      DIMENSION    DATA(360,4), BATCH(30,4)
C**      DIMENSION    SAMPLE(12), TIME(12), RESIJK(12)
C**      COMMON       /INFO/ DATA, BATCH, TYPE
C**      COMMON       /SCAN/ SAMPLE, TIME, RESIJK
C**      COMMON       /VARS/ MODE, NDATA, NBATCH
C**      COMMON       /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      COMMON       /CHAR/ LF
C**
C**      MODE=MODEX
C**      IF (MODE.EQ.1) WRITE(OUT,2007)
C**      IF (MODE.EQ.2) WRITE(OUT,2008)
C**      DO 219 NX=1,NBATCH
219          CLEAR(NX)=.FALSE.
C**      RUN=0
220      RUN=RUN+1
C**      KOUNT=KOUNT+1
C**      IF (MODE.EQ.1) WRITE(UNIT4,2010) LF,LF,LF,LF,LF,LF,LF,
C**      &                                KOUNT,RUN,LF,LF
C**      IF (MODE.EQ.2) WRITE(UNIT4,2011) LF,LF,LF,LF,LF,LF,LF,
C**      &                                KOUNT,RUN,LF,LF
C**      WRITE(UNIT4,2013) LF,LF,LF
C**      DO 225 NX=1,NBATCH
C**          IF (CLEAR(NX)) GOTO 225
C**          INDEX=IFIX(BATCH(NX,1))
C**          KODEX=IFIX(BATCH(NX,2))
C**          SAMPLX=FLOAT(NX)
C**          CALL VALUES(SAMPLX, NSAMPL)

```

```

      IF (NSAMPL.LE.3) GOTO 224
      CALL SORT(SAMPLE, TIME, NSAMPL)
      CALL MEDIAN(SAMPLE, NSAMPL, RMED)
      CALL ZWSTAT(NSAMPL, RMED, ZVAL, WVAL)
      RSAMPL=FLOAT(NSAMPL)
      ZLIMIT= 0.615 + 0.886*ALOG(RSAMPL)
      WLIMIT=-0.357 + 1.73 *ALOG(RSAMPL)
      IF (ZVAL.LT.ZLIMIT.AND.WVAL.LT.WLIMIT) GOTO 224
      CALL REPORT(INDEX, TYPE(NX), KODEX, NSAMPL)
      CALL CLEAN(SAMPLX, NSAMPL, ZVAL, ZLIMIT)
      GOTO 225
224      IF (MODE.EQ.1) WRITE(UNIT4,2018) LF,LF,INDEX,TYPE(NX),KODEX
      IF (MODE.EQ.2) WRITE(UNIT4,2118) LF,LF,INDEX,TYPE(NX),KODEX
      CLEAR(NX)=.TRUE.
225      CONTINUE
      SUM=0
      DO 226 NX=1,NBATCH
226      IF (.NOT.CLEAR(NX)) SUM=SUM+1
      IF (SUM.NE.0) GOTO 220
      WRITE(OUT,2019)
      RETURN
C**
C**
2007      FORMAT(/3X,'SEARCHING FOR OUTLIERS AMONG SAMPLE COUNTS ...')
2008      FORMAT(/3X,'SEARCHING FOR OUTLIERS AMONG SAMPLE SIE VALUES ...')
2010      FORMAT(A1/A1/A1/A1/A1/A1/A1,I2,'. RUN ',I2,' OF OUTLIER ',
&          'DETECTION AMONG SAMPLE COUNTS'/A1,51('-')/A1)
2011      FORMAT(A1/A1/A1/A1/A1/A1/A1,I2,'. RUN ',I2,' OF OUTLIER ',
&          'DETECTION AMONG SAMPLE SIE VALUES'/A1,55('-')/A1)
2013      FORMAT(A1/A1,'SAMPLE',4X,'CODE',9X,'CONDITION'/
&          A1,6('-'),4X,4('-'),9X,9('-'))
2018      FORMAT(A1/A1,(' ',I3,' '),5X,A1,I5,7X,'NO OUTLIERS (COUNTS)')
2118      FORMAT(A1/A1,(' ',I3,' '),5X,A1,I5,7X,'NO OUTLIERS (SIE VALUES)')
2019      FORMAT(3X,'SEARCH COMPLETED.'/)
      END

      SUBROUTINE      SORT(ARRAY1, ARRAY2, NARRAY)
C**
C**
C**      THIS SUBROUTINE PERMUTES THE FIRST 'NARRAY' ELEMENTS OF
C**      'ARRAY1' INTO ASCENDING ORDER AND PERMUTES THE FIRST
C**      'NARRAY' ELEMENTS OF 'ARRAY2' IN ACCORDANCE WITH THE
C**      PERMUTATION IMPOSED ON 'ARRAY1'. (NOTE: THE FIRST
C**      'NARRAY' ELEMENTS OF 'ARRAY2' MAY NOT BE IN ASCENDING
C**      ORDER UNLIKE 'ARRAY1'.)
C**
C**      DIMENSION      ARRAY1(12), ARRAY2(12)
C**
C**
C**      K=0
230      K=K+1

```

```

      L=K+1
231  IF (ARRAY1(K).LE.ARRAY1(L)) GOTO 232
      STORE=ARRAY1(K)
      ARRAY1(K)=ARRAY1(L)
      ARRAY1(L)=STORE
      STORE=ARRAY2(K)
      ARRAY2(K)=ARRAY2(L)
      ARRAY2(L)=STORE
232  L=L+1
      IF (L.LE.NARRAY) GOTO 231
      IF (K.LT.(NARRAY-1)) GOTO 230
      RETURN
      END

```

```

      SUBROUTINE      MEDIAN(AORDER, NORDER, RMED)
C**
C**
C**      THIS SUBROUTINE EVALUATES THE MEDIAN VALUE OF AN ORDERED
C**      ARRAY OF NUMBERS. (NOTE: THE ARRAY MUST BE ORDERED PRIOR
C**      TO ENTERING THIS SUBROUTINE BY USE OF THE 'SORT' ROUTINE
C**      ABOVE.)
C**
      DIMENSION      AORDER(12)
C**
C**
      IF (MOD(NORDER,2).EQ.0.0) GOTO 233
      K1=(NORDER+1)/2
      RMED=AORDER(K1)
      GOTO 234
233  K2=NORDER/2
      K3=(NORDER+2)/2
      RMED=(AORDER(K2)+AORDER(K3))*0.5
234  RETURN
      END

```

```

      SUBROUTINE      ZWSTAT(NSAMPL, RMED, ZVAL, WVAL)
C**
C**
C**      THIS SUBROUTINE EVALUATES THE Z AND W STATISTICS WHICH
C**      ARE USED TO DETECT THE PRESENCE OF OUTLIERS IN A GROUP
C**      OF DATA WHICH HAVE BEEN SORTED INTO ASCENDING ORDER.
C**
C**
      DIMENSION      SAMPLE(12), TIME(12), RESIJK(12)
      DIMENSION      STORE(12)
      COMMON          /SCAN/ SAMPLE, TIME, RESIJK
C**
C**

```

```

RANGE=SAMPLE(NSAMPL)-SAMPLE(1)
SUM=0.0
KSAMPL=NSAMPL-1
DO 235 I=1,KSAMPL
235     SUM=SUM+I*(NSAMPL-I)*(SAMPLE(I+1)-SAMPLE(I))
    GSTAR=(2*SUM)/(NSAMPL*(NSAMPL-1))
DO 236 I=1,NSAMPL
236     STORE(I)=ABS(SAMPLE(I)-RMED)
    CALL SORT(STORE, RESIJK, NSAMPL)
    ZVAL=STORE(NSAMPL)/GSTAR
    WVAL=RANGE/GSTAR
    RETURN
END

```

```

SUBROUTINE      REPORT(INDEX, TYPEX, KODEX, NSAMPL)
C**
C**
C**      THIS SUBROUTINE REPORTS THE PRESENCE OF OUTLIERS IN A GROUP
C**      OF SAMPLE OBSERVATIONS TO THE APPROPRIATE OUTPUT FILE.
C**      THE OBSERVATIONS ARE LISTED AND THE OUTLIER(S) IS(ARE)
C**      ASTERIXED FOR EASY IDENTIFICATION. SINCE THE 'SAMPLE'
C**      ARRAY WILL CONTAIN CPM VALUES WHEN GROSS COUNTS ARE
C**      BEING PROCESSED, THE VALUES ARE MULTIPLIED BY THE COUNTING
C**      TIMES IN ORDER TO RECOVER THE ORIGINAL GROSS COUNTS.
C**      SINCE THE COUNTING TIMES ARE ALL 1.0 FOR SIE VALUES, THIS
C**      WILL NOT AFFECT THE PROCESSING OF SIE VALUES.
C**
C**      INTEGER      OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      LOGICAL      LF, TYPEX
C**      DIMENSION    SAMPLE(12), TIME(12), RESIJK(12)
C**      COMMON       /SCAN/ SAMPLE, TIME, RESIJK
C**      COMMON       /VARS/ MODE, NDATA, NBATCH
C**      COMMON       /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      COMMON       /CHAR/ LF
C**
C**
C**      IF (MODE.EQ.1) WRITE(UNIT4,2015) LF,LF,INDEX,TYPEX,KODEX,LF
C**      IF (MODE.EQ.2) WRITE(UNIT4,2115) LF,LF,INDEX,TYPEX,KODEX,LF
C**      CALL RESIDU(NSAMPL)
C**      DO 237 I=1,NSAMPL
C**          OBSN=SAMPLE(I)*TIME(I)
C**          IF (RESIJK(I).LT.2.0) WRITE(UNIT4,2016) LF,OBSN
C**          IF (RESIJK(I).GT.2.0) WRITE(UNIT4,2017) LF,OBSN
237      CONTINUE
C**      RETURN
C**
C**      2015      FORMAT(A1/A1,('I3,')',5X,A1,I5,7X,'OUTLIER(S) PRESENT ',
C**      &          '(COUNTS)'/A1)
C**      2115      FORMAT(A1/A1,('I3,')',5X,A1,I5,7X,'OUTLIER(S) PRESENT ',
C**      &          '(SIE VALUES)'/A1)

```

```

2016  FORMAT(A1,23X,F9.0)
2017  FORMAT(A1,23X,F9.0,' *')
      END

```

SUBROUTINE RESIDU(NSAMPL)

```

C**
C**
C**      THIS SUBROUTINE EVALUATES A JACK-KNIFE RESIDUAL FOR
C**      EACH SAMPLE OBSERVATION. IT IS BASED ON ABSOLUTE(SAMPLE
C**      VALUE - JACK-KNIFE MEDIAN) STANDARDISED BY THE
C**      JACK-KNIFE GSTAR-STATISTIC.
C**
C**
      DIMENSION  SAMPLE(12), TIME(12), RESIJK(12)
      DIMENSION  STORE(12)
      COMMON     /SCAN/ SAMPLE, TIME, RESIJK
C**
C**
      K=0
238    K=K+1
      L=0
      DO 239 I=1,NSAMPL
          IF (I.EQ.K) GOTO 239
          L=L+1
          STORE(L)=SAMPLE(I)
239    CONTINUE
      SUM=0.0
      KSAMPL=NSAMPL-2
      DO 240 I=1,KSAMPL
240    SUM=SUM+I*(NSAMPL-1-I)*(STORE(I+1)-STORE(I))
      GJACK=(2*SUM)/((NSAMPL-1)*(NSAMPL-2))
      CALL MEDIAN(STORE, NSAMPL-1, RMEDJ)
      RESIJK(K)=(ABS(SAMPLE(K)-RMEDJ))/GJACK
      RETURN
      END

```

SUBROUTINE CLEAN(SAMPLX, NSAMPL, ZVAL, ZLIMIT)

```

C**
C**
C**      THIS SUBROUTINE REMOVES OUTLYING OBSERVATIONS FROM THE DATA
C**      BY ASSIGNING A NUMERICAL VALUE OF ZERO TO ANY OUTLIERS.
C**
C**
      REAL      LOWER
      LOGICAL   TYPE(30)
      DIMENSION DATA(360,4), BATCH(30,4)
      DIMENSION SAMPLE(12), TIME(12), RESIJK(12)
      COMMON    /INFO/ DATA, BATCH, TYPE
      COMMON    /SCAN/ SAMPLE, TIME, RESIJK

```

```

COMMON      /VARS/ MODE, NDATA, NBATCH

C**
C**
      LOWER=SAMPLE(1)
      UPPER=SAMPLE(NSAMPL)
      CALL SORT(RESIJK, SAMPLE, NSAMPL)
      XTREME=SAMPLE(NSAMPL)

C**
C**
C**      IF THE Z STATISTIC IS NOT SIGNIFICANT ('ZVAL.LT.ZLIMIT')
C**      THEN ONLY THE W STATISTIC IS SIGNIFICANT AND AN OUTLIER
C**      PAIR (UPPER AND LOWER) IS REMOVED.
C**
C**
      IF (ZVAL.GE.ZLIMIT) GOTO 344
      DO 343 NX=1,NDATA
        IF (DATA(NX,1).NE.SAMPLX) GOTO 343
        GOTO (341,342),MODE
      341      SVALUE=DATA(NX,3)/DATA(NX,2)
        IF (SVALUE.EQ.UPPER.OR.SVALUE.EQ.LOWER) DATA(NX,3)=0.0
        GOTO 343
      342      SVALUE=DATA(NX,4)
        IF (SVALUE.EQ.UPPER.OR.SVALUE.EQ.LOWER) DATA(NX,4)=0.0
      343      CONTINUE
      GOTO 345

C**
C**
C**      IF THE Z STATISTIC IS SIGNIFICANT ('ZVAL.GE.ZLIMIT')
C**      THEN THE MOST EXTREME OBSERVATION IS REMOVED.
C**
C**
      344      CONTINUE
      DO 243 NX=1,NDATA
        IF (DATA(NX,1).NE.SAMPLX) GOTO 243
        GOTO (241,242),MODE
      241      SVALUE=DATA(NX,3)/DATA(NX,2)
        IF (SVALUE.EQ.XTREME) DATA(NX,3)=0.0
        GOTO 243
      242      SVALUE=DATA(NX,4)
        IF (SVALUE.EQ.XTREME) DATA(NX,4)=0.0
      243      CONTINUE
      345      RETURN
      END

      SUBROUTINE      NEWDAT

C**
C**
C**      THIS SUBROUTINE WRITES THE OUTLIER-FREE DATA TO THE
C**      APPROPRIATE OUTPUT FILE.
C**
C**
      INTEGER      OUT, UNIT1, UNIT2, UNIT3, UNIT4

```

```

LOGICAL      LF, TYPE(30)
DIMENSION    DATA(360,4), BATCH(30,4)
COMMON       /INFO/ DATA, BATCH, TYPE
COMMON       /VARS/ MODE, NDATA, NBATCH
COMMON       /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
COMMON       /CHAR/ LF

C**
C**
WRITE(OUT,2020)
WRITE(UNIT3,2021) (LF,(DATA(I,J),J=1,4),I=1,NDATA)
WRITE(OUT,2022)
RETURN

C**
C**
2020  FORMAT(/3X,'SENDING CLEAN DATA TO FILE ...')
2021  FORMAT(A1,F3.0,1X,F7.2,1X,F8.0,1X,F5.0)
2022  FORMAT(3X,'WRITING COMPLETED.')
```

```

END

SUBROUTINE    AVRAGE(KOUNT)

C**
C**
C**          THIS SUBROUTINE EVALUATES AND REPORTS SIMPLE AVERAGES AND
C**          ERRORS OF AVERAGES FOR ALL SAMPLES WITH RESPECT TO BOTH
C**          SAMPLE CPM AND SIE VALUES.
C**
C**
INTEGER       OUT, UNIT1, UNIT2, UNIT3, UNIT4
LOGICAL       LF
COMMON       /VARS/ MODE, NDATA, NBATCH
COMMON       /UNIT/IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
COMMON       /CHAR/LF

C**
C**
WRITE(OUT,2023)
KOUNT=KOUNT+1
WRITE(UNIT4,2024) LF,LF,LF,LF,LF,LF,LF,LF,KOUNT,LF,LF,LF,LF,LF
DO 244 NX=1,NBATCH
244   CALL AVCALC(NX)
WRITE(OUT,2028)
RETURN

C**
C**
2023  FORMAT(/3X,'CALCULATING SAMPLE MEANS ...')
2024  FORMAT(A1/A1/A1/A1/A1/A1/A1,I2,'. MEANS FOR SAMPLE SIE AND ',
&      'CPM VALUES'/A1,39('-')/A1/A1/A1,'SAMPLE',5X,'CODE',7X,
&      'MEAN SIE ( ERROR) N.',6X,'MEAN CPM ( ERROR) N. '/
&      A1,6('-'),5X,4('-'),7X,20('-'),6X,20('-'))
2028  FORMAT(3X,'CALCULATIONS COMPLETED.'/)
END
```

```

SUBROUTINE      AVCALC(NX)

C**
C**
C**      THIS SUBROUTINE CALCULATES AND REPORTS AVERAGES FOR
C**      CPM AND SIE VALUES FOR A PARTICULAR SAMPLE.
C**      MEAN CPM VALUES ARE STORED IN THE 'AVSMPL' ARRAY TO
C**      BE USED WHEN PRODUCING A BATCH ESTIMATE FOR THE
C**      BACKGROUND LEVEL.
C**

      INTEGER      OUT, UNIT1, UNIT2, UNIT3, UNIT4
      LOGICAL      LF, FLAG1, FLAG2, FLAG3, FLAG4, TYPE(30)
      DIMENSION    DATA(360,4), BATCH(30,4)
      DIMENSION    AVSMPL(30,2)
      COMMON       /INFO/ DATA, BATCH, TYPE
      COMMON       /STAT/ AVSMPL
      COMMON       /VARS/ MODE, NDATA, NBATCH
      COMMON       /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
      COMMON       /CHAR/ LF

C**
C**
      SAMPLX=FLOAT(NX)
      INDEX=IFIX(BATCH(NX,1))
      KODEX=IFIX(BATCH(NX,2))
      MODE=2
      CALL VALUES(SAMPLX, NSIE)
      IF (NSIE.LT.2) GOTO 245
      CALL AVSTAN(NSIE, AVSIE, SDSIE)
      ERRSIE=SDSIE/SQRT(FLOAT(NSIE))
245  CONTINUE
      MODE=1
      CALL VALUES(SAMPLX, NCPM)
      IF (NCPM.LT.2) GOTO 246
      CALL AVSTAN(NCPM, AVCPM, SDCPM)
      ERRCPM=SDCPM/SQRT(FLOAT(NCPM))
      AVSMPL(NX,1)=AVCPM
      AVSMPL(NX,2)=SDCPM
246  CONTINUE
      FLAG1=NSIE.LT.2.AND.NCPM.LT.2
      FLAG2=NSIE.GE.2.AND.NCPM.LT.2
      FLAG3=NSIE.LT.2.AND.NCPM.GE.2
      FLAG4=NSIE.GE.2.AND.NCPM.GE.2
      IF (FLAG1) WRITE(UNIT4,2026) LF,LF,INDEX,TYPE(NX),KODEX
      IF (FLAG2) WRITE(UNIT4,2126) LF,LF,INDEX,TYPE(NX),KODEX,
&                                AVSIE,ERRSIE,NSIE
      IF (FLAG3) WRITE(UNIT4,2226) LF,LF,INDEX,TYPE(NX),KODEX,
&                                AVCPM,ERRCPM,NCPM
      IF (FLAG4) WRITE(UNIT4,2326) LF,LF,INDEX,TYPE(NX),KODEX,
&                                AVSIE,ERRSIE,NSIE,AVCPM,ERRCPM,NCPM
      RETURN

C**
C**
2026  FORMAT(A1/A1,(' ',I3,')',6X,A1,I5,6X,'INSUFFICIENT VALUES',
&          7X,'INSUFFICIENT VALUES')

```

```

2126  FORMAT(A1/A1,('I3,')',6X,A1,I5,4X,F9.3,1X,('F6.3,')',1X,I2,
&      7X,'INSUFFICIENT VALUES')
2226  FORMAT(A1/A1,('I3,')',6X,A1,I5,6X,'INSUFFICIENT VALUES',
&      5X,F9.3,1X,('F6.3,')',1X,I2)
2326  FORMAT(A1/A1,('I3,')',6X,A1,I5,4X,F9.3,1X,('F6.3,')',1X,I2,
&      5X,F9.3,1X,('F6.3,')',1X,I2)
      END

```

SUBROUTINE BACKGR(KOUNT)

```

C**
C**
C**      THIS SUBROUTINE EVALUATES AND REPORTS THE BACKGROUND LEVEL
C**      BASED ON ALL BACKGROUND SAMPLES EXCLUDING ANY DELETED BY
C**      REQUEST AT THE BEGINNING OF THE PROGRAM'S RUN. A LOWER
C**      LIMIT IS PERMITTED FOR THE ERROR OF THE BATCH ESTIMATE
C**      OF THE BACKGROUND, THIS BEING DEFINED BY 'BLIMIT' —
C**      SEE BLOCK DATA SUBPROGRAM 'BLOCK2'.
C**
C**

```

```

      INTEGER      OUT, UNIT1, UNIT2, UNIT3, UNIT4
      INTEGER      BDLETE(6)
      LOGICAL      LF, DELETE, XDLETE
      LOGICAL      BKTYPE, OXTYPE, FSTYPE, TYPE(30)
      DIMENSION    DATA(360,4), BATCH(30,4)
      DIMENSION    SAMPLE(12), TIME(12), RESIJK(12)
      DIMENSION    AVSMPL(30,2)
      COMMON        /INFO/ DATA, BATCH, TYPE
      COMMON        /SCAN/ SAMPLE, TIME, RESIJK
      COMMON        /STAT/ AVSMPL
      COMMON        /OPTN/ DELETE, BDLETE, NDLETE
      COMMON        /TYP5/ BKTYPE, OXTYPE, FSTYPE
      COMMON        /VARS/ MODE, NDATA, NBATCH
      COMMON        /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
      COMMON        /CHAR/ LF
      COMMON        /BLIM/ BLIMIT

```

```

C**
C**
      WRITE(OUT,2029)
      KOUNT=KOUNT+1
      IX=0
      WRITE(UNIT4,2030) LF,LF,LF,LF,LF,LF,LF,KOUNT,LF,LF,LF,LF,LF,LF
      DO 253 NX=1,NBATCH
        IF (TYPE(NX).NE.BKTYPE) GOTO 253
        KODEX=IFIX(BATCH(NX,2))
        IF (AVSMPL(NX,1).EQ.0.0) GOTO 251
        IF (.NOT.DELETE) GOTO 250
        XDLETE=.FALSE.
        DO 249 JX=1,NDLETE
          249      IF (BDLETE(JX).EQ.KODEX) XDLETE=.TRUE.
        IF (XDLETE) GOTO 252
        250      IX=IX+1
        SAMPLE(IX)=AVSMPL(NX,1)

```

```

WRITE(UNIT4,2032) LF,LF,TYPE(NX),KODEX,(AVSMPL(NX,J),J=1,2)
GOTO 253
251  WRITE(UNIT4,2033) LF,LF,TYPE(NX),KODEX
GOTO 253
252  WRITE(UNIT4,2034) LF,LF,TYPE(NX),KODEX
253  CONTINUE
      NBACK=IX
      IF (NBACK.LT.2) GOTO 254
      CALL AVSTAN(NBACK, BACK, ERBKB)
      IF (ERBKB.LT.BLIMIT) ERBKB=BLIMIT
      WRITE(UNIT4,2035) LF,LF,LF,LF,NBACK,LF,LF,BACK,LF,LF,ERBKB
      GOTO 255
254  WRITE(UNIT4,2036) LF,LF,LF,LF
255  WRITE(OUT,2037)
      RETURN
C**
C**
2029  FORMAT(/3X,'CALCULATING MEAN BACKGROUND ...')
2030  FORMAT(A1/A1/A1/A1/A1/A1,I2,' MEAN BACKGROUND LEVEL'/
&      A1,25('-')/A1/A1/A1,'CODE',7X,'MEAN CPM',1X,
&      '( ERROR)'/A1,4('-'),7X,17('-')/A1)
2032  FORMAT(A1/A1,A1,I5,7X,F6.3,1X,('F6.3,')')
2033  FORMAT(A1/A1,A1,I5,8X,'NOT ENOUGH OBS')
2034  FORMAT(A1/A1,A1,I5,8X,'DELETED SAMPLE')
2035  FORMAT(A1/A1/A1/A1,'NO. OF SAMPLES  = ',4X,I2/
&      A1/A1,'MEAN BACKGROUND = ',F6.3/
&      A1/A1,'STANDARD ERROR  = ',F6.3)
2036  FORMAT(A1/A1/A1/A1,'INSUFFICIENT SAMPLES FOR POOLING')
2037  FORMAT(3X,'CALCULATION COMPLETED.'/)
      END

```

B Age Program

```
C**
C**
C**      BRIEF DESCRIPTION OF 'AGEPROG2.FOR'
C**
C**
C**
C**
C**      AUTHOR: ALISTER T. HOOKE
C**      DATE   : OCTOBER, 1991
C**
C**
C**      LEGEND: (M)=MAIN PROGRAM ROUTINE;
C**              (S)=SUBROUTINE SUBPROGRAM;
C**              (B)=BLOCK DATA SUBPROGRAM.
C**
C**
C**      LIST OF ROUTINES IN ORDER OF APPEARANCE :-
C**          (1)   'AGE'   (M) — TOP LEVEL MANAGEMENT OF AGE PROGRAM;
C**          (2)   'INBACK' (S) — READS IN NET BACKGROUND AND ERROR;
C**          (3)   'INQUEN' (S) — READS IN QUENCH CURVE DATA;
C**          (4)   'INPURE' (S) — READS IN OUTLIER-FREE BATCH DATA;
C**          (5)   'OXALIC' (S) — ESTIMATES QUENCH VALUES AND MODERN
C**                               ACTIVITIES OF ALL STANDARD SAMPLES;
C**          (6)   'QUVALU' (S) — ESTIMATES SAMPLE QUENCH VALUE;
C**          (7)   'QCURVE' (S) — OBTAINS SAMPLE QUENCH VALUE FROM
C**                               REGRESSION CURVE;
C**          (8)   'ACTVTY' (S) — ESTIMATES SAMPLE ACTIVITY;
C**          (9)   'OXMEAN' (S) — ESTIMATES NET MODERN ACTIVITY;
C**          (10)  'FIELDS' (S) — ESTIMATES QUENCH VALUES, ACTIVITIES,
C**                               PERCENT MODERNS AND C14 AGES FOR ALL
C**                               FIELD SAMPLES;
C**          (11)  'AGESMP' (S) — CALCULATES C14 AGE OF SAMPLE;
C**          (12)  'PERSMP' (S) — CALCULATES PERCENT MODERN OF SAMPLE.
C**
C**
C**      LIST OF ROUTINES SHARED WITH THE OUTLIER PROGRAM
C**      (THESE ROUTINES ARE CURRENTLY LOCATED IN 'SHARED.FOR') :-
C**          (1)   'BLOCK1' (B) — INITIALISES MAIN ROUTINE VARIABLES;
C**          (2)   'BLOCK2' (B) — INITIALISES MISCELLANEOUS VARIABLES;
C**          (3)   'INAUXI' (S) — READS IN AUXILIARY BATCH DATA;
C**          (4)   'VALUES' (S) — PICKS OUT ALL VALUES CORRESPONDING
C**                               TO A PARTICULAR SAMPLE;
C**          (5)   'AVSTAN' (S) — CALCULATES MEAN AND STANDARD ERROR
C**                               FOR AN ARRAY OF VALUES.
C**
C**
C**
C**      NOTE: MORE DETAILED DESCRIPTIONS, INCLUDING DESCRIPTIONS OF
C**      MAIN VARIABLES, ARE PROVIDED IN THE COMMENTS APPEARING AT THE
C**      BEGINNING OF EACH ROUTINE.
C**
C**
```

PROGRAM AGE

```
C**
C**
C**      MAIN PROGRAM ROUTINE FOR CALCULATING THE RADIOCARBON
C**      AGES OF ALL FIELD SAMPLES.
C**      NOTE: THE VARIABLES IN THIS MAIN ROUTINE ARE DESCRIBED
C**      AND INITIALISED IN THE BLOCK DATA SUBPROGRAM 'BLOCK1'
C**      WHICH IS CURRENTLY LOCATED IN THE FILE 'SHARED.FOR'.
C**
C**      EXTERNAL    BLOCK1, BLOCK2
C**      INTEGER     DRIVE, OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      REAL*8      FILE1(2), FILE2(2), FILE3(2)
C**      REAL*8      FILE4(2), FILE5(2), FILE6(2)
C**      LOGICAL     LF
C**      COMMON      /DISK/ DRIVE
C**      COMMON      /FILE/ FILE1, FILE2, FILE3, FILE4, FILE5, FILE6
C**      COMMON      /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      COMMON      /CHAR/ LF
C**
C**
C**      OPEN ALL INPUT AND OUTPUT FILES. THE RELEVANT FILES ARE :-
C**      (1) AUXILIARY DATA FILE      (INPUT FILE='FILE1')
C**      (2) QUENCH CURVE DATA FILE   (INPUT FILE='FILE2')
C**      (3) OUTLIER-FREE DATA FILE   (OUTPUT FILE='FILE4')
C**      (4) C14 AGES REPORT FILE      (OUTPUT FILE='FILE6')
C**
C**      CALL OPEN(UNIT1, FILE1, DRIVE)
C**      CALL OPEN(UNIT2, FILE2, DRIVE)
C**      CALL OPEN(UNIT3, FILE4, DRIVE)
C**      CALL OPEN(UNIT4, FILE6, DRIVE)
C**
C**
C**      BEGIN PROCESSING :-
C**      (1) 'INBACK' READS IN NET BACKGROUND AND ERROR FROM SCREEN;
C**      (2) 'INQUEN' READS IN QUENCH CURVE DATA (FILE='FILE2');
C**      (3) 'INAUX1' READS IN AUXILIARY BATCH DATA (FILE='FILE1');
C**      (4) 'INPURE' READS IN OUTLIER-FREE BATCH DATA (FILE='FILE4');
C**      (5) 'OXALIC' ESTIMATES QUENCH VALUES AND ACTIVITIES OF ALL
C**          STANDARD SAMPLES;
C**      (6) 'OXMEAN' ESTIMATES THE NET MODERN ACTIVITY USING
C**          WEIGHTED LEAST SQUARES WITH COVARIANCES;
C**      (7) 'FIELDS' ESTIMATES QUENCH VALUES, ACTIVITIES, PERCENT
C**          MODERNS AND C14 AGES FOR ALL FIELD SAMPLES.
C**      NOTE: (5), (6) AND (7) EACH REPORT TO THE SAME OUTPUT FILE
C**          (FILE='FILE6').
C**
C**      CALL INBACK
C**      CALL INQUEN
```

SUBROUTINE INQUEN

```

C**
C**
C**      THIS SUBROUTINE READS IN THE QUENCH CURVE DATA. THIS DATA
C**      IS THE DATA PERTAINING TO A QUADRATIC REGRESSION OF THE
C**      COUNTING ACTIVITIES ON THE SIE VALUES FOR A SERIES OF
C**      SPIKED SAMPLES. THE DATA CONSISTS OF THE COEFFICIENTS OF
C**      THE REGRESSION ('A','B','C' WHERE 'Y=A+B*X+C*X**2'), THE SIX
C**      ELEMENTS OF THE INVERSE COVARIANCE MATRIX ('V1' -> 'V6'),
C**      THE BASELINE SIE VALUE ('BSIE') WHICH IS THE SIE OF AN
C**      UNQUENCHED SAMPLE, THE STANDARD ERROR OF THE FITTED CURVE
C**      ('SDFIT') AND A DIVISION FACTOR ('DIV') WHICH IS USED TO
C**      STANDARDISE THE SIE VALUES.
C**
C**
C**      INTEGER      OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      LOGICAL      DUMMY, LF
C**      COMMON       /QCH1/ A, B, C, V1, V2, V3, V4, V5, V6
C**      COMMON       /QCH2/ BSIE, SDFIT, DIV
C**      COMMON       /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      COMMON       /CHAR/ LF
C**
C**
C**      WRITE(OUT,2003)
C**      READ(UNIT2,1100) DUMMY
C**      READ(UNIT2,1001,ERR=406) A,B,C,V1,V2,V3,V4,V5,V6,
&      BSIE,SDFIT,DIV
C**      WRITE(OUT,2004)
C**      WRITE(UNIT4,2104) LF,LF,LF,LF,LF,LF,A,LF,B,LF,C,LF,V1,LF,V2,LF,
&      V3,LF,V4,LF,V5,LF,V6,LF,BSIE,LF,SDFIT,LF,DIV
C**      GOTO 407
406  WRITE(OUT,3001)
      STOP
407  RETURN
C**
C**
1100  FORMAT(A1)
1001  FORMAT(6X,F12.3)
2003  FORMAT(/3X,'READING IN QUENCH CURVE DATA ...')
2004  FORMAT(A1/A1/A1,'QUENCH DATA'/A1,11('-')/A1/A1,'A   ',F12.3/
&      A1,'B   ',F12.3/A1,'C   ',F12.3/A1,'V1  ',F12.3/
&      A1,'V2  ',F12.3/A1,'V3  ',F12.3/A1,'V4  ',F12.3/
&      A1,'V5  ',F12.3/A1,'V6  ',F12.3/A1,'BASE=',F12.3/
&      A1,'SD   ',F12.3/A1,'DIV  ',F12.3)
3001  FORMAT(/3X,'*** READING ERROR *** CHECK FORMAT OF DATA.'/)
      END

```

SUBROUTINE INPURE

```

C**
C**
C**      THIS SUBROUTINE READS IN THE OUTLIER-FREE BATCH DATA.
C**      EACH DATA RECORD CONSISTS OF :-
C**          (1) SAMPLE NUMBER;
C**          (2) SAMPLE COUNTING TIME;
C**          (3) SAMPLE GROSS COUNT VALUE;
C**          (4) SAMPLE SIE VALUE.
C**      THE DATA ARE STORED IN THE 'DATA' ARRAY AND THE NUMBER
C**      OF DATA RECORDS IS RECORDED IN 'NDATA'.
C**

```

```

C**      INTEGER      OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      LOGICAL      LF, RECORD(30), TYPE(30)
C**      DIMENSION    DATA(360,4), BATCH(30,4)
C**      COMMON       /INFO/ DATA, BATCH, TYPE
C**      COMMON       /VARS/ MODE, NDATA, NBATCH
C**      COMMON       /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4

```

```

C**
C**      WRITE(OUT,2005)
C**      NR=0
408  READ(UNIT3,1002,END=409) (RECORD(I),I=1,30)
C**      NR=NR+1
C**      DECODE(RECORD,1003) (DATA(NR,J),J=1,4)
C**      GOTO 408
409  NDATA=NR
C**      IF (NDATA.EQ.0) GOTO 410
C**      WRITE(OUT,2006)
C**      GOTO 411
410  WRITE(OUT,3002)
C**      STOP
411  RETURN

```

```

C**
C**      1002  FORMAT(30A1)
C**      1003  FORMAT(F3.0,1X,F7.2,1X,F8.0,1X,F5.0)
C**      2005  FORMAT(/3X,'READING IN OUTLIER-FREE DATA ...')
C**      2006  FORMAT(3X,'DATA RECEIVED.')
```

```

C**      3002  FORMAT(/3X,'*** DATA FILE EMPTY ***  PROGRAM STOPPED.')
```

```

SUBROUTINE      OXALIC

```

```

C**
C**
C**      THIS SUBROUTINE ESTIMATES THE QUENCH VALUES AND ACTIVITIES
C**      OF ALL STANDARD SAMPLES. IT ALSO STORED DATA FOR THE PURPOSE
C**      OF ESTIMATING THE NET MODERN ACTIVITY. THESE DATA ARE :-
C**          (1) 'VECTOX' — CPM VALUES MINUS NET BACKGROUND;
C**          (2) 'VECVAR' — INVERSE VARIANCES OF CPM VALUES;
C**          (3) 'GAMMOX' — INVERSE GAMMA VALUES WHERE GAMMA IS
C**                        QUENCH*FRACTIONATION/WEIGHT(SAMPLE BENZENE);

```

```

C**      (4) 'GAMVAR' — VARIANCES OF INVERSE GAMMA VALUES;
C**      (5) 'NOXSMP' — TOTAL NUMBER OF STANDARD SAMPLES;
C**      (6) 'NOX' — TOTAL NUMBER OF CPM VALUES FOR SAMPLE;
C**      (7) 'NOXOBS' — TOTAL NUMBER OF CPM VALUES OVER ALL
C**                      STANDARD SAMPLES.
C**
C**      INTEGER      OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      LOGICAL      LF, INSUFF
C**      LOGICAL      BKTYPE, OXTYPE, FSTYPE, TYPE(30)
C**      DIMENSION    DATA(360,4), BATCH(30,4)
C**      DIMENSION    SAMPLE(12), TIME(12), RESIJK(12)
C**      DIMENSION    VECTOX(72), VECVAR(72), GAMMOX(72), GAMVAR(72)
C**      DIMENSION    NOX(6)
C**      COMMON       /INFO/ DATA, BATCH, TYPE
C**      COMMON       /SCAN/ SAMPLE, TIME, RESIJK
C**      COMMON       /OXAL/ VECTOX, VECVAR, GAMMOX, GAMVAR, NOX
C**      COMMON       /ONET/ OXNET, ERROX, NOXOBS, NOXSMP
C**      COMMON       /MEAN/ BACK, ERBK, QUENCH, ERRQU, ACTIV, ERRAC
C**      COMMON       /VALU/ GAMMA, SDCPM, NCPM, NSIE
C**      COMMON       /TYP/ BKTYPE, OXTYPE, FSTYPE
C**      COMMON       /VAR/ MODE, NDATA, NBATCH
C**      COMMON       /AGES/ FACTOR, ACONST
C**      COMMON       /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      COMMON       /CHAR/ LF
C**
C**
C**      WRITE(OUT,2007)
C**      WRITE(UNIT4,2008) LF,LF,LF,LF,LF,LF,LF,LF,LF,LF,LF,LF,LF
C**      NOXOBS=0
C**      KOXSMP=0
C**      KSTART=0
C**      KFINIS=0
C**      DO 413 NX=1,NBATCH
C**          IF (TYPE(NX).NE.OXTYPE) GOTO 413
C**          SAMPLX=FLOAT(NX)
C**          KODEX=IFIX(BATCH(NX,2))
C**          INSUFF=.FALSE.
C**          CALL QUVALU(SAMPLX, NX, OXTYPE, KODEX, INSUFF)
C**          IF (INSUFF) GOTO 413
C**          CALL ACTVTY(SAMPLX, OXTYPE, KODEX, INSUFF)
C**          IF (INSUFF) GOTO 413
C**          ACTIVF=FACTOR*ACTIV
C**          ERRACF=FACTOR*ERRAC
C**          WRITE(UNIT4,2011) LF,LF,TYPE(NX),KODEX,
C**      &                      QUENCH,ERRQU,NSIE,
C**      &                      ACTIVF,ERRACF,NCPM
C**          KSTART=NOXOBS+1
C**          KFINIS=NOXOBS+NCPM
C**          DO 412 IX=KSTART,KFINIS
C**              KX=IX-KSTART+1
C**              VECTOX(IX)=SAMPLE(KX)-BACK
C**              VECVAR(IX)=1.0/SDCPM**2
C**              GAMMOX(IX)=1.0/GAMMA
C**              GAMVAR(IX)=ERRQU**2/(QUENCH**2*GAMMA**2)

```

```

412          CONTINUE
             KOXSMP=KOXSMP+1
             NOXOBS=NOXOBS+NCPM
             NOX(KOXSMP)=NCPM
413          CONTINUE
             NOXSMP=KOXSMP
             WRITE(OUT,2012)
             RETURN

C**
C**
2007  FORMAT(/3X,'PROCESSING STANDARD SAMPLES ...')
2008  FORMAT(A1/A1/A1/A1/A1/A1/A1,'2. MODERN ACTIVITIES',
&      ' INCLUDING NET MODERN ACTIVITY'/A1,50('-')/
&      A1/A1/A1,'SAMPLE',3X,'QUENCH (ERROR ) N.',
&      3X,'ACTVTY (ERROR) N.'/A1,6('-'),3X,18('-'),3X,17('-'))
2011  FORMAT(A1/A1,A1,I5,3X,F6.4,1X,('F6.4, '),1X,I2,
&      3X,F6.3,1X,('F5.3, '),1X,I2)
2012  FORMAT(3X,'PROCESS COMPLETED.'/)
      END

SUBROUTINE    QUVALU(SAMPLX, NX, TYPEX, KODEX, INSUFF)

C**
C**
C**          THIS SUBROUTINE ESTIMATES THE SAMPLE QUENCH VALUE. THE SAMPLE
C**          QUENCH VALUE AND ERROR ARE STORED RESPECTIVELY IN 'QUENCH'
C**          AND 'ERRQU'. THE SAMPLE GAMMA VALUE IS STORED IN 'GAMMA'.
C**          THE LOGICAL VARIABLE 'INSUFF' ASSESSES WHETHER THERE
C**          ARE SUFFICIENT VALUES OR NOT TO ESTIMATE THE QUENCH VALUE.
C**
C**
      INTEGER    OUT, UNIT1, UNIT2, UNIT3, UNIT4
      LOGICAL    LF, INSUFF, TYPEX, TYPE(30)
      DIMENSION  DATA(360,4), BATCH(30,4)
      COMMON     /INFO/ DATA, BATCH, TYPE
      COMMON     /MEAN/ BACK, ERBK, QUENCH, ERRQU, ACTIV, ERRAC
      COMMON     /VALU/ GAMMA, SDCPM, NCPM, NSIE
      COMMON     /VARS/ MODE, NDATA, NBATCH
      COMMON     /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
      COMMON     /CHAR/ LF

C**
C**
      MODE=2
      CALL VALUES(SAMPLX, NSIE)
      IF (NSIE.LT.2) GOTO 414
      CALL QCURVE
      WEIGHT=BATCH(NX,3)
      FRACTN=BATCH(NX,4)
      GAMMA=QUENCH*FRACTN/WEIGHT
      GOTO 415
414  INSUFF=.TRUE.
      WRITE(UNIT4,2009) LF,LF,TYPEX,KODEX
415  RETURN

```

```

C**
C**
2009  FORMAT(A1/A1,A1,I5,4X,'NOT ENOUGH VALUES')
      END

```

```

      SUBROUTINE      QCURVE

C**
C**
C**      THIS SUBROUTINE OBTAINS THE SAMPLE QUENCH VALUE AND ERROR
C**      FROM THE REGRESSION CURVE OUTLINED IN THE SUBROUTINE 'INQUEN'.
C**
C**
      DIMENSION      SAMPLE(12), TIME(12), RESIJK(12)
      COMMON          /SCAN/ SAMPLE, TIME, RESIJK
      COMMON          /QCH1/ A, B, C, V1, V2, V3, V4, V5, V6
      COMMON          /QCH2/ BSIE, SDFIT, DIV
      COMMON          /MEAN/ BACK, ERRBK, QUENCH, ERRQU, ACTIV, ERRAC
      COMMON          /VALU/ GAMMA, SDCPM, NCPM, NSIE

C**
C**
      XSMPL=0.0
      DO 501 I=1,NSIE
501      XSMPL=XSMPL+SAMPLE(I)
      XSMPL=XSMPL/(NSIE*DIV)
      XBASE=BSIE/DIV
      YSMPL=A+B*XSMPL+C*XSMPL**2
      YBASE=A+B*XBASE+C*XBASE**2
      QUENCH=YBASE/YSMPL
      VSMPL=V1+2*V2*XSMPL+(2*V3+V4)*XSMPL**2+2*V5*XSMPL**3+V6*XSMPL**4
      VBASE=V1+2*V2*XBASE+(2*V3+V4)*XBASE**2+2*V5*XBASE**3+V6*XBASE**4
      ESMPL=SDFIT*SQRT(VSMPL)
      EBASE=SDFIT*SQRT(VBASE)
      ERRQU=QUENCH*SQRT(ESMPL**2/YSMPL**2+EBASE**2/YBASE**2)
      RETURN
      END

```

```

      SUBROUTINE      ACTVTY(SAMPLX, TYPEX, KODEX, INSUFF)

C**
C**
C**      THIS SUBROUTINE ESTIMATES SAMPLE ACTIVITY AND STORES
C**      ESTIMATE IN 'ACTIV' AND ERROR IN 'ERRAC'.
C**      'INSUFF' IS USED IN THE SAME WAY AS FOR THE SAMPLE
C**      QUENCH VALUE.
C**
C**
      INTEGER          OUT, UNIT1, UNIT2, UNIT3, UNIT4
      LOGICAL          LF, INSUFF, TYPEX
      COMMON          /MEAN/ BACK, ERRBK, QUENCH, ERRQU, ACTIV, ERRAC
      COMMON          /VALU/ GAMMA, SDCPM, NCPM, NSIE

```

```

COMMON      /VARS/  MODE, NDATA, NBATCH
COMMON      /UNIT/  IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
COMMON      /CHAR/  LF

C**
C**

MODE=1
CALL VALUES(SAMPLX, NCPM)
IF (NCPM.LT.2) GOTO 514
CALL AVSTAN(NCPM, AVCPM, SDCPM)
ACTIV=(AVCPM-BACK)*GAMMA
ERRAV=SDCPM/SQRT(FLOAT(NCPM))
ERRAC=(ERRAV**2+ERRBK**2)/(AVCPM-BACK)**2
ERRAC=ERRAC+ERRQU**2/QUENCH**2
ERRAC=ACTIV*SQRT(ERRAC)
GOTO 515

514  INSUFF=.TRUE.
      WRITE(UNIT4,2010) LF,LF,TYPEX,KODEX,QUENCH,ERRQU,NSIE
515  RETURN

C**
C**
2010  FORMAT(A1/A1,A1,I5,3X,F6.4,1X,('F6.4, '),1X,I2,4X,
&      'NOT ENOUGH VALUES')
      END

SUBROUTINE    OXMEAN

C**
C**
C**      THIS SUBROUTINE ESTIMATES THE NET MODERN ACTIVITY AND
C**      AND ERROR USING WEIGHTED LEAST SQUARES WITH COVARIANCES.
C**      THE VECTORS 'AOX1' AND 'AOX2' ARE RESPECTIVELY <THE
C**      INVERSE COVARIANCE MATRIX OF CPM VALUES MINUS BACKGROUND>
C**      TIMES <THE CPM VALUES MINUS BACKGROUND> AND <THE SAME
C**      MATRIX> TIMES <THE INVERSE GAMMA VALUES>. THE VARIABLE
C**      'V' IS <THE INVERSE GAMMA VALUES> TIMES 'AOX2'.
C**      BOTH 'AOX2' AND 'V' ARE REQUIRED IN THE ESTIMATION OF
C**      THE COVARIANCE BETWEEN THE NET MODERN ACTIVITY AND
C**      FIELD SAMPLES IN THE CALCULATION OF THE ERROR OF THE
C**      C14 AGES. THE NET STANDARD ACTIVITY AND ERROR ARE
C**      STORED RESPECTIVELY IN 'OXNET' AND 'ERROX'.
C**
C**

INTEGER      OUT, UNIT1, UNIT2, UNIT3, UNIT4
LOGICAL      LF
DIMENSION    VECTOX(72), VECVAR(72), GAMMOX(72), GAMVAR(72)
DIMENSION    NOX(6)
DIMENSION    AOX1(72), AOX2(72)
COMMON      /OXAL/  VECTOX, VECVAR, GAMMOX, GAMVAR, NOX
COMMON      /AOXV/  AOX2, V, COVAR
COMMON      /ONET/  OXNET, ERROX, NOXOBS, NOXSMP
COMMON      /MEAN/  BACK, ERBK, QUENCH, ERRQU, ACTIV, ERRAC
COMMON      /AGES/  FACTOR, ACONST
COMMON      /UNIT/  IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4

```

```

COMMON      /CHAR/ LF
C**
C**
      WRITE(OUT,2013)
      IF (NOXSMP.EQ.0) GOTO 423
C**
C**
      CALCULATE NET MODERN ACTIVITY.
C**
C**
      OXSUM=0.0
      DO 417 I=1,NOXOBS
1417      OXSUM=OXSUM+VECVAR(I)
      OXSUM=OXSUM+1.0/ERRBK**2
      U=0.0
      V=0.0
      DO 419 I=1,NOXOBS
          SUM1=0.0
          SUM2=0.0
          DO 418 J=1,NOXOBS
              IF (I.EQ.J) SIGMOX=VECVAR(I)-VECVAR(I)**2/OXSUM
              IF (I.NE.J) SIGMOX=-VECVAR(I)*VECVAR(J)/OXSUM
              SUM1=SUM1+SIGMOX*VECTOX(J)
              SUM2=SUM2+SIGMOX*GAMMOX(J)
1418          CONTINUE
          AOX1(I)=SUM1
          AOX2(I)=SUM2
          U=U+GAMMOX(I)*AOX1(I)
          V=V+GAMMOX(I)*AOX2(I)
1419      CONTINUE
      OXNET=U/V
      OXNETF=FACTOR*OXNET
C**
C**
      CALCULATE ERROR OF NET MODERN ACTIVITY.
C**
C**
      ERROX=0.0
      MOXOBS=0
      DO 422 I=1,NOXSMP
          JLIMIT=NOX(I)
          DO 421 J=1,JLIMIT
              KS=MOXOBS+1
              KE=MOXOBS+NOX(I)
              SUM=0.0
              DO 420 K=1,NOXOBS
                  IF (K.GE.KS.AND.K.LE.KE) G=GAMVAR(K)
                  IF (K.LT.KS.OR .K.GT.KE) G=0.0
                  SUM=SUM+G*(V*AOX1(K)-2.0*U*AOX2(K))/V**2
1420              CONTINUE
              L=MOXOBS+J
              ERROX=ERROX+SUM*(V*AOX1(L)-2.0*U*AOX2(L))/V**2
1421          CONTINUE
          MOXOBS=MOXOBS+NOX(I)
1422      CONTINUE

```

```

ERROX=SQRT(1.0/V+ERROX)
ERROXF=FACTOR*ERROX

C**
C**
WRITE(UNIT4,2015) LF,LF,LF,LF,NOXSMP,LF,LF,OXNETF,LF,LF,ERROXF
GOTO 424
423 WRITE(UNIT4,2016) LF,LF,LF
424 WRITE(OUT,2017)
RETURN

C**
C**
2013 FORMAT(/3X,'PRODUCING NET ESTIMATE OF MODERN ACTIVITY ...')
2015 FORMAT(A1/A1/A1/A1,'NO. OF POOLED SAMPLES = ',4X,I2/A1/A1,
&      'NET MODERN ACTIVITY = ',F6.3/A1/A1,
&      'ERROR OF NET ACTIVITY = ',F6.3)
2016 FORMAT(A1/A1/A1,'INSUFFICIENT SAMPLES FOR POOLING')
2017 FORMAT(3X,'ESTIMATION COMPLETED.'/)
END

SUBROUTINE      FIELDS

C**
C**
C**      THIS SUBROUTINE CALCULATES SEVERAL VALUES FOR EACH
C**      FIELD SAMPLE. THESE VALUES ARE :-
C**      (1) QUENCH VALUE AND ERROR ('QUENCH' & 'ERRQU');
C**      (2) SAMPLE ACTIVITY AND ERROR ('ACTIV' & 'ERRAC');
C**      (3) PERCENT MODERN AND ERROR ('PERCNT' & 'ERRPC');
C**      (4) C14 AGE AND ERROR ('IAGE' & 'IERRAG').
C**
C**
C**      INTEGER      OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      LOGICAL      LF, INSUFF
C**      LOGICAL      BKTYPE, OXTYPE, FSTYPE, TYPE(30)
C**      DIMENSION    DATA(360,4), BATCH(30,4)
C**      COMMON       /INFO/ DATA, BATCH, TYPE
C**      COMMON       /ONET/ OXNET, ERROX, NOXOBS, NOXSMP
C**      COMMON       /MEAN/ BACK, ERRBK, QUENCH, ERRQU, ACTIV, ERRAC
C**      COMMON       /VALU/ GAMMA, SDCPM, NCPM, NSIE
C**      COMMON       /TYP/  BKTYPE, OXTYPE, FSTYPE
C**      COMMON       /VAR/  MODE, NDATA, NBATCH
C**      COMMON       /AGE/  FACTOR, ACONST
C**      COMMON       /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      COMMON       /CHAR/ LF

C**
C**
WRITE(OUT,2018)
WRITE(UNIT4,2019) LF,LF,LF,LF,LF,LF,LF,LF,LF,LF
WRITE(UNIT4,2020) LF,LF,LF
DO 425 NX=1,NBATCH
    IF (TYPE(NX).NE.FSTYPE) GOTO 425
    SAMPLX=FLOAT(NX)
    KODEX=IFIX(BATCH(NX,2))

```

```

      INSUFF=.FALSE.
      CALL QUVALU(SAMPLX, NX, FSTYPE, KODEX, INSUFF)
      IF (INSUFF) GOTO 425
      CALL ACTVTY(SAMPLX, FSTYPE, KODEX, INSUFF)
      IF (INSUFF) GOTO 425
      IF (NOXSMP.EQ.0) GOTO 525
      CALL AGESMP(IAGE, IERRAG)
      CALL PERSMP(PERCNT, ERRPC)
      WRITE(UNIT4,2021) LF,LF,TYPE(NX),KODEX,QUENCH,ERRQU,NSIE,
&          ACTIV,ERRAC,NCPM,PERCNT,ERRPC,IAGE,IERRAG
      GOTO 425
525      WRITE(UNIT4,2022) LF,LF,TYPE(NX),KODEX,QUENCH,ERRQU,NSIE,
&          ACTIV,ERRAC,NCPM
425      CONTINUE
      WRITE(OUT,2023)
      RETURN
C**
C**
2018      FORMAT(/3X,'PROCESSING FIELD SAMPLES ...')
2019      FORMAT(A1/A1/A1/A1/A1/A1/A1,'3. FIELD SAMPLE STATISTICS'/
&          A1,26('-')/A1)
2020      FORMAT(A1/A1,'SAMPLE',3X,'QUENCH (ERROR ) N.',3X,
&          'ACTVTY (ERROR) N.',3X,'PERCNT (ERR.)',3X,'C14AGE (ERR.)'/
&          A1,6('-'),3X,18('-'),3X,17('-'),3X,13('-'),3X,13('-'))
2021      FORMAT(A1/A1,A1,I5,3X,F6.4,1X,('F6.4,')',1X,I2,3X,F6.3,1X,('F5.3,')',1X,I2,3X,F6.2,1X,('F4.2,')',3X,I6,1X,('I4,')')
&          F5.3,')',1X,I2,3X,F6.2,1X,('F4.2,')',3X,I6,1X,('I4,')')
2022      FORMAT(A1/A1,A1,I5,3X,F6.4,1X,('F6.4,')',1X,I2,3X,F6.3,1X,
&          ('F5.3,')',1X,I2,3X,'NET MODERN IS UNAVAILABLE')
2023      FORMAT(3X,'PROCESS COMPLETED.'/)
      END

      SUBROUTINE      AGESMP(IAGE, IERRAG)
C**
C**
C**      THIS SUBROUTINE CALCULATES THE C14 AGE OF A SAMPLE
C**      TAKING INTO ACCOUNT COVARIANCES AMONG OBSERVATIONS.
C**
C**
      DIMENSION      AOX2(72)
      COMMON          /AOXV/ AOX2, V, COVAR
      COMMON          /ONET/ OXNET, ERROX, NOXOBS, NOXSMP
      COMMON          /MEAN/ BACK, ERBBK, QUENCH, ERRQU, ACTIV, ERRAC
      COMMON          /VALU/ GAMMA, SDCPM, NCPM, NSIE
      COMMON          /AGES/ FACTOR, ACONST
C**
C**
      AGE=ACONST*ALOG(FACTOR*OXNET/ACTIV)
      BIT=AGE-FLOAT(IFIX(AGE))
      IF (BIT.LT.0.5) IAGE=IFIX(AGE)
      IF (BIT.GE.0.5) IAGE=IFIX(AGE)+1
      COVAR=0.0
      DO 428 I=1,NOXOBS

```

```

428      COVAR=COVAR+ERRBK**2*GAMMA*AOX2(I)/V
      ERRAG=ERROX**2/OXNET**2+ERRAC**2/ACTIV**2
      ERRAG=ERRAG-2*COVAR/(OXNET*ACTIV)
      ERRAG=ACONST*SQRT(ERRAG)
      IERRAG=IFIX(ERRAG)+1
      RETURN
      END

```

```

      SUBROUTINE      PERSMP(PERCNT, ERRPC)

C**
C**
C**      THIS SUBROUTINE CALCULATES THE PERCENT MODERN OF A SAMPLE
C**      TAKING INTO ACCOUNT COVARIANCES AMONG OBSERVATIONS.
C**

      DIMENSION      AOX2(72)
      COMMON          /AOXV/ AOX2, V, COVAR
      COMMON          /ONET/ OXNET, ERROX, NOXOBS, NOXSMP
      COMMON          /MEAN/ BACK, ERRBK, QUENCH, ERRQU, ACTIV, ERRAC
      COMMON          /AGES/ FACTOR, ACONST

C**
C**
      PERCNT=100.0*ACTIV/(FACTOR*OXNET)
      ERRPC=ERROX**2/OXNET**2+ERRAC**2/ACTIV**2
      ERRPC=ERRPC-2*COVAR/(OXNET*ACTIV)
      ERRPC=PERCNT*SQRT(ERRPC)
      RETURN
      END

```

C Shared Routines

```
C**
C**
C**      BRIEF DESCRIPTION OF 'SHARED.FOR'
C**      _____
C**
C**
C**      AUTHOR: ALISTER T. HOOKE
C**      DATE   : OCTOBER, 1991
C**
C**
C**      LEGEND: (B)=BLOCK DATA SUBPROGRAM;
C**              (S)=SUBROUTINE SUBPROGRAM.
C**
C**
C**      LIST OF ROUTINES IN ORDER OF APPEARANCE :-
C**          (1)  'BLOCK1' (B) — INITIALISES VARIABLES BELONGING
C**                      TO MAIN PROGRAM ROUTINES OF BOTH
C**                      THE OUTLIER AND AGE PROGRAMS;
C**          (2)  'BLOCK2' (B) — INITIALISES VARIOUS MISCELLANEOUS
C**                      VARIABLES APPEARING THROUGHOUT BOTH
C**                      THE OUTLIER AND AGE PROGRAMS;
C**          (3)  'INAUX1' (S) — READS IN AUXILIARY BATCH DATA;
C**          (4)  'VALUES' (S) — PICKS OUT ALL VALUES CORRESPONDING
C**                      TO A PARTICULAR SAMPLE;
C**          (5)  'AVSTAN' (S) — CALCULATES MEAN AND STANDARD ERROR
C**                      FOR AN ARRAY OF VALUES.
C**
C**
C**      NOTE: THESE ROUTINES ARE ALL SHARED BY THE OUTLIER AND AGE
C**      PROGRAMS.
C**
C**
```

BLOCK DATA BLOCK1

```
C**
C**
C**      FIX MAIN ROUTINE VARIABLES FOR OUTLIER AND AGE PROGRAMS :-
C**          (1)  'DRIVE' = DISK DRIVE ON WHICH I/O FILES ARE LOCATED;
C**          (2)  'FILE1' = AUXILIARY DATA FILE (INPUT FILE);
C**          (3)  'FILE2' = QUENCH CURVE DATA FILE (INPUT FILE);
C**          (4)  'FILE3' = UNPROCESSED DATA FILE (INPUT FILE);
C**          (5)  'FILE4' = OUTLIER-FREE DATA FILE (INPUT FILE);
C**          (6)  'FILE5' = OUTLIER REPORT FILE (OUTPUT FILE);
C**          (7)  'FILE6' = RADIOCARBON AGES REPORT FILE (OUTPUT FILE);
C**          (8)  'UNIT1' = UNIT FOR READING IN 'FILE1';
C**          (9)  'UNIT2' = UNIT FOR READING IN 'FILE2' AND 'FILE3';
C**          (10) 'UNIT3' = UNIT FOR READING IN AND WRITING TO 'FILE4';
```

```

C**      (11) 'UNIT4' = UNIT FOR WRITING TO 'FILE5' AND 'FILE6';
C**      (12) 'IN' = UNIT FOR READING IN FROM THE SCREEN;
C**      (13) 'OUT' = UNIT FOR WRITING TO THE SCREEN;
C**      (14) 'LF' = LINE FEED CHARACTER (USED IN WRITING TO FILES).
C**
C**

```

```

INTEGER    DRIVE, OUT, UNIT1, UNIT2, UNIT3, UNIT4
REAL*8     FILE1(2), FILE2(2), FILE3(2)
REAL*8     FILE4(2), FILE5(2), FILE6(2)
LOGICAL    LF
COMMON     /DISK/ DRIVE
COMMON     /FILE/ FILE1, FILE2, FILE3, FILE4, FILE5, FILE6
COMMON     /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4
COMMON     /CHAR/ LF

```

```

C**
C**
C**      ASSIGN VALUES ACCORDING TO THE PARTICULAR OPERATING SYSTEM.
C**
C**

```

```

DATA       DRIVE /2/
DATA       FILE1 /'AUXIDATA', 'DAT'/
DATA       FILE2 /'QUENDATA', 'DAT'/
DATA       FILE3 /'ORIGDATA', 'DAT'/
DATA       FILE4 /'PUREDATA', 'DAT'/
DATA       FILE5 /'OUTLIERS', 'REP'/
DATA       FILE6 /'C14-AGES', 'REP'/
DATA       UNIT1, UNIT2 /6, 7/
DATA       UNIT3, UNIT4 /8, 9/
DATA       IN, OUT /3, 5/
DATA       LF /10/
END

```

```

BLOCK DATA    BLOCK2

```

```

C**
C**
C**      FIX MISCELLANEOUS VARIABLES APPEARING THROUGHOUT
C**      BOTH THE OUTLIER AND AGE PROGRAMS :-
C**      (1) 'BKTYPE' = SYMBOL FOR BACKGROUND SAMPLES;
C**      (2) 'OXTYPE' = SYMBOL FOR OXALIC SAMPLES;
C**      (3) 'FSTYPE' = SYMBOL FOR FIELD SAMPLES;
C**      (4) 'PRNUM' = PROTOCOL NUMBER CORRESPONDING TO COUNTER;
C**      (5) 'NTH' = POSITION OF PROTOCOL NUMBER IN DATA RECORD;
C**      (6) 'BLIMIT' = LOWEST ERROR PERMISSIBLE FOR NET BACKGROUND;
C**      (7) 'FACTOR' = ADJUSTMENT TO NET OXALIC VALUE;
C**      (8) 'ACONST' = AGE CONSTANT.
C**      NOTE: SYMBOLS (1), (2) AND (3) MUST CORRESPOND TO THOSE
C**      APPEARING IN THE AUXILIARY BATCH DATA FILE.
C**
C**

```

```

LOGICAL    BKTYPE, OXTYPE, FSTYPE
COMMON     /TYP/ BKTYPE, OXTYPE, FSTYPE
COMMON     /PNUM/ PRNUM, NTH

```

```

COMMON      /BLIM/ BLIMIT
COMMON      /AGES/ FACTOR, ACONST

C**
C**

DATA        BKTYPE, OXTYPE, FSTYPE /'B', 'M', 'G'/
DATA        PRONUM, NTH /'1', 5/
DATA        BLIMIT /0.075/
DATA        FACTOR, ACONST /0.7459, 8033.0/
END

SUBROUTINE   INAUXI

C**
C**
C**      THIS SUBROUTINE READS IN AUXILIARY BATCH DATA.
C**      EACH DATA RECORD CONTAINS :-
C**          (1) SAMPLE NUMBER (1,2,3,...);
C**          (2) SAMPLE TYPE ('B'=BACKGROUND,...);
C**          (3) SAMPLE CODE (INTEGER FOR IDENTIFYING SAMPLE);
C**          (4) SAMPLE BENZENE WEIGHT IN GRAMS;
C**          (5) SAMPLE FRACTIONATION VALUE.
C**      THE AUXILIARY DATA IS STORED IN THE 'BATCH' ARRAY WITH THE
C**      EXCEPTION OF SAMPLE TYPE WHICH IS STORED IN THE 'TYPE' ARRAY.
C**      THE NUMBER OF SAMPLES TO BE PROCESSED IS RECORDED IN
C**      'NBATCH'.
C**
C**      INTEGER      OUT, UNIT1, UNIT2, UNIT3, UNIT4
C**      LOGICAL      RECORD(30), TYPE(30)
C**      DIMENSION    DATA(360,4), BATCH(30,4)
C**      COMMON       /INFO/ DATA, BATCH, TYPE
C**      COMMON       /VARS/ MODE, NDATA, NBATCH
C**      COMMON       /UNIT/ IN, OUT, UNIT1, UNIT2, UNIT3, UNIT4

C**
C**      WRITE(OUT,2000)
C**      NR=0
201  READ(UNIT1,1000,END=202) (RECORD(I),I=1,30)
      NR=NR+1
      DECODE(RECORD,1001) BATCH(NR,1),TYPE(NR),(BATCH(NR,J),J=2,4)
      GOTO 201
202  NBATCH=NR
      IF (NBATCH.EQ.0) GOTO 302
      WRITE(OUT,2001)
      GOTO 303
302  WRITE(OUT,2001)
      STOP
303  RETURN

C**
C**
1000  FORMAT(30A1)
1001  FORMAT(F3.0,1X,A1,1X,F5.0,1X,F5.3,1X,F6.4)
2000  FORMAT(/3X,'READING AUXILIARY DATA FILE ...')

```

```

2001  FORMAT(3X,'DATA RECEIVED.')
```

```

3000  FORMAT(/3X,'*** AUXILIARY FILE EMPTY ***  PROGRAM STOPPED.'//)
      END
```

SUBROUTINE VALUES(SAMPLX, NSAMPL)

```

C**
C**
C**      THIS SUBROUTINE PICKS OUT ALL OBSERVATIONS —
C**      COUNTS ('MODE'=1) OR SIE VALUES ('MODE'=2) —
C**      PERTAINING TO THE SAMPLE DENOTED BY 'SAMPLX'. THE
C**      COUNTS ARE STANDARDISED TO COUNTS PER MINUTE (CPM) TO
C**      ALLOW A PROPER COMPARISON BETWEEN THE OBSERVATIONS.
C**      THE RELEVANT OBSERVATIONS ARE STORED IN THE 'SAMPLE'
C**      ARRAY AND THE SAMPLE COUNTING TIMES ARE STORED IN
C**      THE 'TIME' ARRAY IN ORDER TO RECOVER THE ORIGINAL
C**      COUNTS. WHEN SIE VALUES ARE BEING PROCESSED
C**      THE TIMES ARE ALL SET TO AN ARTIFICIAL VALUE OF 1.0.
C**      THE NUMBER OF OBSERVATIONS — COUNTS OR SIE VALUES —
C**      BELONGING TO A SAMPLE IS RECORDED IN 'NSAMPL'. ZERO
C**      VALUES INDICATE THAT AN OUTLIER HAS BEEN DETECTED
C**      AND SUCH VALUES ARE IGNORED HERE.
C**
C**
```

```

      LOGICAL      TYPE(30)
      DIMENSION    DATA(360,4), BATCH(30,4)
      DIMENSION    SAMPLE(12), TIME(12), RESIJK(12)
      COMMON       /INFO/ DATA, BATCH, TYPE
      COMMON       /SCAN/ SAMPLE, TIME, RESIJK
      COMMON       /VARS/ MODE, NDATA, NBATCH
```

```

C**
C**
```

```

      IX=0
      DO 229 NX=1,NDATA
        IF (DATA(NX,1).NE.SAMPLX) GOTO 229
        IF (MODE.EQ.1.AND.DATA(NX,3).EQ.0.0) GOTO 229
        IF (MODE.EQ.2.AND.DATA(NX,4).EQ.0.0) GOTO 229
        IX=IX+1
        GOTO (227,228),MODE
227      SAMPLE(IX)=DATA(NX,3)/DATA(NX,2)
        TIME(IX)=DATA(NX,2)
        GOTO 229
228      SAMPLE(IX)=DATA(NX,4)
        TIME(IX)=1.0
229      CONTINUE
      NSAMPL=IX
      RETURN
      END
```

SUBROUTINE AVSTAN(N, AV, SD)

```

C**
C**
C**      THIS SUBROUTINE EVALUATES MEANS AND STANDARD ERRORS
C**      FOR AN ARRAY OF DATA VALUES.
C**
      DIMENSION  SAMPLE(12), TIME(12), RESIJK(12)
      COMMON     /SCAN/ SAMPLE, TIME, RESIJK
C**
C**
      AV=0.0
      SD=0.0
      DO 247 I=1,N
247      AV=AV+SAMPLE(I)
      AV=AV/N
      DO 248 I=1,N
248      SD=SD+(SAMPLE(I)-AV)**2
      SD=SQRT(SD/(N-1))
      RETURN
      END

```

D Example of Outlier Program Report

1. RUN 1 OF OUTLIER DETECTION AMONG SAMPLE COUNTS

<u>SAMPLE</u>	<u>CODE</u>	<u>CONDITION</u>
(1)	B 206	NO OUTLIERS (COUNTS)
(2)	M 68	OUTLIER(S) PRESENT (COUNTS)
		127.*
		2043.
		2127.
		2133.
		2163
		2190.
		2192.
		2201.
		2220.
(3)	G 3046	NO OUTLIERS (COUNTS)
(4)	G 3047	NO OUTLIERS (COUNTS)
(5)	G 3048	NO OUTLIERS (COUNTS)
(6)	B 212	NO OUTLIERS (COUNTS)
(7)	M 69	NO OUTLIERS (COUNTS)
(8)	G 3049	NO OUTLIERS (COUNTS)
(9)	G 3053	NO OUTLIERS (COUNTS)
(10)	G 3054	NO OUTLIERS (COUNTS)
(11)	B 213	NO OUTLIERS (COUNTS)
(12)	M 71	NO OUTLIERS (COUNTS)
(13)	G 3055	NO OUTLIERS (COUNTS)
(14)	B 257	NO OUTLIERS (COUNTS)
(15)	B 258	NO OUTLIERS (COUNTS)
(16)	M 72	NO OUTLIERS (COUNTS)
(17)	G 2179	NO OUTLIERS (COUNTS)
(18)	S 2	NO OUTLIERS (COUNTS)
(19)	G 3082	NO OUTLIERS (COUNTS)
(20)	G 3083	NO OUTLIERS (COUNTS)

2. RUN 2 OF OUTLIER DETECTION AMONG SAMPLE COUNTS

<u>SAMPLE</u>	<u>CODE</u>	<u>CONDITION</u>
(2)	M 68	NO OUTLIERS (COUNTS)

3. RUN 1 OF OUTLIER DETECTION AMONG SAMPLE SIE VALUES

<u>SAMPLE</u>	<u>CODE</u>	<u>CONDITION</u>
(1)	B 206	NO OUTLIERS (SIE VALUES)
(2)	M 68	NO OUTLIERS (SIE VALUES)
		16.*
		607.
		611.
		612.

612.
613.
614.
619.
620.

(3)	G 3046	NO OUTLIERS (SIE VALUES)
(4)	G 3047	NO OUTLIERS (SIE VALUES)
(5)	G 3048	NO OUTLIERS (SIE VALUES)
(6)	B 212	NO OUTLIERS (SIE VALUES)
(7)	M 69	NO OUTLIERS (SIE VALUES)
(8)	G 3049	NO OUTLIERS (SIE VALUES)
(9)	G 3053	NO OUTLIERS (SIE VALUES)
(10)	G 3054	NO OUTLIERS (SIE VALUES)
(11)	B 213	NO OUTLIERS (SIE VALUES)
(12)	M 71	NO OUTLIERS (SIE VALUES)
(13)	G 3053	NO OUTLIERS (SIE VALUES)
(14)	B 257	NO OUTLIERS (SIE VALUES)
(15)	B 258	NO OUTLIERS (SIE VALUES)
(16)	M 72	NO OUTLIERS (SIE VALUES)
(17)	G 2179	NO OUTLIERS (SIE VALUES)
(18)	S 2	NO OUTLIERS (SIE VALUES)
(19)	G 3082	NO OUTLIERS (SIE VALUES)
(20)	G 3083	NO OUTLIERS (SIE VALUES)

4. RUN 2 OF OUTLIER DETECTION AMONG SAMPLE SIE VALUES

<u>SAMPLE</u>	<u>CODE</u>	<u>CONDITION</u>
(2)	M 68	NO OUTLIERS (SIE VALUES)

5. MEANS FOR SAMPLE SIE AND CPM VALUES

<u>SAMPLE</u>	<u>CODE</u>	<u>MEAN SIE</u>	<u>(ERROR)</u>	<u>N.</u>	<u>MEAN CPM</u>	<u>(ERROR)</u>	<u>N.</u>
(1)	B 206	554.600	(.763)	10	6.040	(.084)	10
(2)	M 68	613.500	(1.500)	8	53.9669	(.503)	8
(3)	G 3046	610.600	(.980)	10	33.240	(.258)	10
(4)	G 3047	626.600	(1.249)	10	28.067	(.203)	10
(5)	G 3048	599.300	(1.212)	10	23.630	(.230)	10
(6)	B 212	553.900	(1.005)	10	5.955	(.075)	10
(7)	M 69	624.600	(1.024)	10	57.353	(.221)	10
(8)	G 3049	618.700	(1.212)	10	25.235	(.209)	10
(9)	G 3053	632.100	(.795)	10	31.068	(.232)	10
(10)	G 3054	611.900	(.924)	10	38.335	(.289)	10
(11)	B 213	562.400	(.777)	10	6.092	(.078)	10
(12)	M 71	602.300	(.920)	10	57.790	(.571)	10
(13)	G 3055	587.500	(.637)	10	21.907	(.253)	10
(14)	B 257	584.900	(.888)	10	5.848	(.084)	10
(15)	B 258	587.600	(.718)	10	6.118	(.087)	10
(16)	M 72	625.600	(.792)	10	57.908	(.271)	10
(17)	G 2179	573.100	(1.402)	10	38.225	(.349)	10
(18)	S 2	536.600	(.702)	10	11682.662	(36.044)	10
(19)	G 3082	593.900	(.605)	10	15.623	(.140)	10
(20)	G 3083	579.100	(.781)	10	19.578	(.177)	10

6. MEAN BACKGROUND LEVEL

<u>CODE</u>	<u>MEAN CPM</u>	<u>(ERROR)</u>
B 206	6.040	(.084)
B 212	5.955	(.075)
B 213	6.092	(.078)
B 257	5.848	(.084)
B 258	6.118	(.087)

NO. OF SAMPLES = 5
MEAN BACKGROUND = 6.011
STANDARD ERROR = .110

END OF REPORT

E Example of Age Program Report

1. INPUT STATISTICS

BACKGROUND AND ERROR

6.011 (.110)

QUENCH DATA

A = -1629.100
B = 15298.900
C = -11327.500
V1 = 55.148
V2 = -179.581
V3 = 142.588
V4 = 588.256
V5 = -469.893
V6 = 377.840
BASE = 600.000
SD = 17.140
DIV = 1000.000

2. MODERN ACTIVITIES INCLUDING MEAN MODERN ACTIVITY

<u>SAMPLE</u>	<u>QUENCH (ERROR)</u>	<u>N.</u>	<u>ACTIVITY (ERROR)</u>	<u>N.</u>
M 68	.9940 (.0017)	8	8.433 (.092)	8
M 69	.9900 (.0018)	10	8.294 (.043)	10
M 71	.9989 (.0017)	10	8.446 (.096)	10
M 72	.9897 (.0018)	10	8.377 (.049)	10

NO. OF POOLED SAMPLES = 4

MEAN MODERN ACTIVITY = 8.344

ERROR OF MEAN ACTIVITY = .033

3. FIELD SAMPLE STATISTICS

<u>SAMPLE</u>	<u>QUENCH (ERROR)</u>	<u>N.</u>	<u>ACTIVITY (ERROR)</u>	<u>N.</u>	<u>PERCNT (ERR.)</u>	<u>C14AGE (ERR.)</u>
G 3046	.9952 (.0017)	10	6.033 (.063)	10	72.30 (.75)	2605 (84)
G 3047	.9894 (.0018)	10	4.848 (.051)	10	58.10 (.60)	4362 (83)
G 3048	1.0003 (.0017)	10	3.912 (.057)	10	46.88 (.66)	6086 (114)
G 3049	.9920 (.0017)	10	4.439 (.055)	10	53.20 (.64)	5070 (97)
G 3053	.9877 (.0018)	10	5.664 (.059)	10	67.88 (.69)	3112 (83)
G 3054	.9946 (.0017)	10	7.128 (.069)	10	85.42 (.83)	1266 (79)
G 3055	1.0067 (.0017)	10	5.340 (.093)	10	64.00 (1.09)	3585 (137)
G 2179	1.0158 (.0017)	10	7.267 (.083)	10	87.09 (1.00)	1110 (93)
G 3082	1.0031 (.0017)	10	7.885 (.147)	10	94.49 (1.67)	455 (142)
G 3083	1.0118 (.0017)	10	4.352 (.067)	10	52.15 (.77)	5229 (119)

END OF REPORT

References

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